Catalytic behavior of Cu, Ag and Au nanoparticles
A comparison

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1 Introduction

What are you exactly doing? This is a frequently asked question, followed by the request to explain it in a simple ay, so everybody can understand it. Indeed only a small group op researchers is involved in catalysis and know what it is all about, including the applications and possibilities of catalysis. Although catalysis is not well known to the public, it is very important for the production of many industrial products, chemicals and for environmental protection.

In principle, catalysis is a technology, which speeds up a chemical reaction, by use of a catalyst. A catalyst, therefore, is the material used for this increase in reaction rate, by lowering the activation energy and, very importantly, the catalyst can do that without being consumed. Catalysis also provides an enhanced selectivity or specificity to particular products which are more desirable than others, which makes products more economically feasible. In chemistry, catalysis is roughly divided into two research fields. One being homogeneous catalysis in which the catalyst and reactants are in the same phase(mostly liquid), the other is heterogeneous catalysis, in which the catalyst and reactants are in different phases. In most cases the heterogeneous catalyst is a solid powder and the reactants are gases.

In 1836 Berzelius was the first who used the word catalysis in a concept of a

"Catalytic Force" which drives chemical reactions. But long before that catalytic processes were in use, especially in production of wine and beer (yeast). Since the times of Berzelius more and more applications have been found of catalytic processes. Nowadays catalysis is essential for various crucial processes and reactions. It is essential for catalytic converters in automobiles, reducing emissions of carbon monoxide, NO_x and hydrocarbons. However, catalysis is also essential in production of gasoline from crude oil, and removing the sulfur from fuel. In the future automobiles will probably run on clean energy, such as fuel cells, hydrogen or biomass. This is not possible without the use of catalysis.

Gasoline is just one example of a product in which catalysis in needed. The production of propane, butane, plastics, synthetic rubbers, cosmetics and polymers such as adhesives, coatings, foams, and packaging materials, textile and industrial fibers, composites, electronic devices, biomedical devices, optical devices are not economically possible without catalysis. Next to chemical processes, a very important class of catalysts are enzymes. Like all catalysts, enzymes work by lowering the activation energy. However, enzymes do differ from most other catalysts by being much more specific.

Due to the development of new and improved characterization methods, our understanding of heterogeneous catalysis is advancing. Especially the understanding in formation of products from partial oxidation or dehydrogenation. As those products are often required, rather than the products of total oxidation or hydrogenation, hence CO_2 and water.

1.1 Composition of catalysts

The catalysts used in heterogeneous catalysis are mostly solids and are composed of multiple compounds. The greatest part is the support. In most cases this is a cheap, solid with a high surface area per gram and no catalytic activity (i.e. γ-Al_2O_3, SiO_2, carbon nanotubes, zeolites). On this support a catalytically active metal or metal oxide is deposited in low concentrations. For this component especially the transition metals oxides or the noble metals can be used. The catalytic process is taking place on these components. More complex catalysts also contain extra components to improve the activity and selectivity to the desired products. These components can be divided into different classes. For instance structural promoters, which play a role in stabilization of the catalysts and improve the lifetime of the catalyst.
A second class are the co-catalysts or cooperative catalysts [1]. These compounds

assist in the chemical catalytic process by cooperating with the catalytic metal by, for example, providing active oxygen. A third class are chemical promoters. By itself the promoter has little or no catalytic effect. Some promoters interact with active components of catalysts and thereby alter their chemical effect on the catalyzed substance. The interaction may cause changes in the electronic or crystal structures of the active solid component. Commonly used promoters are metal ions incorporated into metals and metal oxide catalysts, reducing and oxidizing gases or liquids, and acids and bases added during the reaction or to the catalysts before being used. The additive may also poison the catalyst surface in a selective way. Usually, catalyst poisoning is undesirable as it leads to a loss of usefulness of expensive noble metals or their complexes. However, poisoning of catalysts can be used to improve selectivities of reactions. In case of multiple competing reactions, one can poison a specific catalytic center for one reaction, so an other reaction can proceed more easily, resulting in a more selective catalyst. In the classical "Rosenmund reduction" of acyl chlorides to aldehydes, the palladium catalyst (over barium sulfate or calcium carbonate) is poisoned by the addition of sulfur or quinoline. This system reduces triple bonds faster than double bonds allowing for an especially selective reduction. Lindlar's catalyst is another example: palladium poisoned with lead salts.

1.2 The use of gold in catalysis

It has been shown in 1987 by Haruta et al. [2] that gold nano-particles (particles smaller than 15 nm in diameter) are active in the low temperature oxidation of CO. Until then, only very little research has been done in the field of gold catalysts, because they were considered inactive due to small chemisorption ability. Gold adsorbs neither hydrogen nor oxygen [3] at ambient temperatures, so it was thought that it cannot be used as a hydrogenation or oxidation catalyst. Therefore only goldsmiths used gold, and today still 70 % of the world's gold production is used for jewellery.

After 1987 a lot of research has been done on highly dispersed gold catalysts. Gold based catalysts have been reported to be active in several other reactions, such as preferential CO oxidation in the presence of H_2 [4, 5], reduction of NO_x [6, 7], and water-gas shift reaction [8]. Recently, it was reported that also unsupported, powdered gold catalysts show activity in CO oxidation [9]. Nevertheless, the best gold catalysts are obtained when the metal is highly dispersed on a metal oxide, such as CeO_x, TiO_2 or MnO_x.

It is generally agreed that small gold particles are essential for the catalysts to

be active. Many studies show that there are large differences in activity between catalysts with large and small gold particles. In general with decreasing particle size the following effects may be considered:

1. A larger fraction of atoms is in contact with the support, which leads to stabilization of the particles. This stabilization has a positive effect on the activity. The length of the interface between gold and support (perimeter) increases as well. It has been suggested that the reaction occurs at this perimeter [10]. In this way the activity increases with decreasing particle size.

2. More steps, edges and kinks on the surface are formed, on which reactions can occur more easily.

The activity of the catalyst is increased by using small particles. However, it should be noted that it is not only the gold particle size that determines the catalyst activity. For example, in the oxidation of carbon monoxide on Au/TiO_2 the oxygen is provided by the support, while CO is adsorbed on the gold particles [6, 10]. Hence, as pointed out by Haruta et al. [11], the Au particle size alone can not account for a high activity. The support and additive materials have an important role as well.

1.3 The effect of addition of metal oxides to gold based catalysts

As was shown by Grisel [12] and Gluhoi [13] the choice of additive or combination of additives is very important for the activity and selectivity of the catalysts. Alkali oxides like Li_2O added to a gold based catalyst act as structural promoter because it the additive stabilize the particle size of the noble metal, it enhances its stability, and it prevents sintering. But lithium oxide not only affects the particle size of gold, it also has a poisoning effect on the acidic sites of the γ-Al_2O_3 support [14] and, hence, can influence the selectivity.

In contrast to promoters, co-catalysts do have an active role in the catalytic process. CeO_x is a well-known co-catalyst, which can be used as a catalyst itself. It is able to oxidize CO and hydrocarbons, although at higher temperatures than noble metal catalysts. Ceria can also store and release oxygen depending on the reaction conditions, due to its facile redox cycle between Ce^{3+} and Ce^{4+} [15].

1.4 Aims of this Thesis

Clearly gold deposited as nanoparticles on a support is a very active catalyst in contrast to bulk gold which does not show any catalytic activity. The question arises if this particle size effect is exclusively valid for gold catalysis or can a similar effect be found in other metals? In the research described in this thesis we investigated copper and silver based catalysts for similar particle size effects as for gold based catalysts. Copper and silver form together with gold group 11 or IB group of periodic table. In contrast to gold bulk silver and copper are known to be active in catalysis and both metals are used as catalysts. Silver is the metal of choice for the formation of ethylene oxide from ethylene but also for the formation of formaldehyde in the BASF process. A Cu/Zn-based catalyst is used for the synthesis of methanol from CO and H_2, and copper-based catalysts are also active in oxidation reactions.

As the interaction between the gold nanoparticles with the additives is very important for the catalytic activity [13],the effect of additions of Li_2O and CeO_x have also been investigated for the silver and copper based catalysts [7, 16]. These additives stabilize the nanoparticles and CeO_x which is known for its oxygen storage and oxidation capacities and is one of the best additives for gold based catalysts [13].

Various oxidation and dehydrogenation reactions have been investigated over copper, silver and gold based catalysts, which are presented in this thesis. In chapter 2 the preferential oxidation of CO is discussed. Chapter 3 deals with the selective oxidation of NH_3. Chapter 4 is devoted to the oxidation and dehydrogenation of methanol. Chapter 5 presents the results of formation of ethylene oxide in the oxidation and dehydrogenation of ethanol on silver and copper based catalysts. In chapter 6 more results of ethanol dehydrogenation and oxidation on gold based catalysts are presented. Chapter 7 gives insight into the activity of gold based catalysts in oxidation and dehydrogenation of 1-propanol and 2-propanol, In the final chapter 8 a general discussion and the conclusions of the most relevant results of the previous chapters are given.

1.5 Publications related to this thesis

Most results of this thesis have also been presented in the following articles:

1. Lippits M.J., Gluhoi A.C., Nieuwenhuys B.E., *A comparative study of the effect of addition of CeO_x and Li_2O on γ-Al_2O_3 supported copper, silver and gold catalysts in the preferential oxidation of CO*, Topics in Catalysis, vol. 44, no. 1-2, p. 159-165. **(chapter 2)**

2. Lippits M.J., Gluhoi A.C., Nieuwenhuys B.E., *A comparative study of the selective oxidation of NH_3 to N_2 over gold, silver and copper catalysts and the effect of addition of Li_2O and CeO_x* , Catalysis Today, vol. 137, no. 2-4, p. 446-452. **(chapter 3)**

3. Lippits M.J., Iwema, R., Nieuwenhuys B.E., *A comparative study of oxidation of methanol on gamma-Al2O3 supported group IB metal catalysts*, Catalysis Today, vol. 145 no. 1, p. 27-33. **(chapter 4)**

4. Lippits M.J., Nieuwenhuys B.E., *Direct conversion of ethanol into ethylene oxide on copper and silver nanoparticles. Effect of addition of CeO_x and Li_2O* , Catalysis Today, 154 (1-2) (2010), p.127-132. **(chapter 5)**

5. Lippits M.J., Nieuwenhuys B.E., *Direct conversion of ethanol into ethylene oxide on gold based catalysts*, Journal of Catalysis vol. 274 no.2 (2010) p.142-149. **(chapter 6)**

6. Lippits M.J., Nieuwenhuys B.E., *Dehydrogenation, dehydration and oxidation of propanol over gold based catalysts*, to be published. **(chapter 7)**

7. Dekkers M.A.P., Lippits M.J., Nieuwenhuys B.E., *Supported gold/MO_x catalysts for NO/H_2 and CO/O_2 reactions*, Catalysis Today, vol. 54 p. 381-390.

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2

A comparative study of the effect of addition of CeO_x and Li_2O on γ-Al_2O_3 supported copper, silver and gold catalysts in the preferential oxidation of CO

In the study described in this paper we deposited gold, silver and copper on γ-Al_2O_3 as nanoparticles (<4nm) and investigated the behavior of these nanoparticles in the preferential oxidation of CO in presence of H_2. In addition, the effect of addition of CeO_x and/or Li_2O was investigated. All the three metals show preferential oxidation of CO at low temperatures. The oxides added to Au/γ-Al_2O_3, Ag/γ-Al_2O_3 and Cu/γ-Al_2O_3 improve the catalytic performance of the gold, silver and copper. Interesting and synergistic effects were observed when both the CeO_x and Li_2O were added. Possible mechanisms are proposed.

2.1 Introduction

The polymer electrolyte fuel cel (PEMFC) can generate electricity without polluting the environment. In this system hydrogen is oxidized over Pt electrodes and electric energy is generated, with ideally the only reaction product being H_2O. The supply of hydrogen needed for operation can be produced from methanol [1, 2] or other fuels [2, 3], via partial oxidation, steam reforming, and/or water gas shift reactions. In the ideal situation the product stream from these reactions consists of only CO_2 and H_2. However, in practice the product stream also contains several vol% H_2O and about 1-2 vol% CO [4]. Especially the presence of CO in the feed causes major problems as Pt is effectively poisoned by CO at the operating temperatures of the fuel cell, i.e. 60-100 °C [5, 6]. In addition, H_2 oxidation will compete with CO oxidation in gas streams containing both compounds. Hence, there is an urgent need to find a way to remove CO selectively from the product stream.

In several papers it is reported that CO can be oxidized in the presence of hydrogen on supported noble metal catalysts such as Pt,Ru and Rh report in the temperature range 100-250°C [7–9]. At lower temperatures the CO oxidation is rather slow due to inhibition of oxygen adsorption by adsorbed CO. At temperatures above 250 °C the selectivity decreases because thermal desorption of CO enables H_2 oxidation.

Highly dispersed gold on suitable metal oxides exhibits extraordinarily high activity in low-temperature CO oxidation [10–14]. In addition, several studies have indicated that the rate of CO oxidation over supported Au catalysts exceeds that of H_2 oxidation [15–17]. Therefore, gold is a promising catalyst for the preferential catalytic oxidation of CO (PROX) in the presence of H_2 in the temperature range up to 100°C. By promoting Au catalysts great improvements in activity can be obtained [13, 15, 16, 18] and the temperature range of CO conversion can be enlarged. Recent studies have shown that also CuO mixed with ZnO [19] and CuO mixed with cerium oxide [20–22] are promising PROX catalysts. A DFT study [23] shows that gold and copper have a lower barrier for CO oxidation than for H_2 oxidation. Previously reported results show that ceria has a promoting effect on the activity of the Au/Al_2O_3 catalyst in CO oxidation [13, 24]. It was argued that the active oxygen is supplied by the ceria. Moreover, it was reported that the size of the ceria particles has a great influence on the activity of the catalyst [25]. A detailed study of Gluhoi et al. [26–28] on the effects of addition of (earth) alkali metals to a Au/Al_2O_3 catalyst revealed that the main role of the (earth) alkali metals is to stabilize the gold nanoparticles i.e. that of a structural promoter in the investigated reactions.

In the present paper a comparative study is described concerning the effect of addition of Li_2O and/or CeO_x to copper, silver and gold catalysts on the preferential oxidation of CO in a hydrogen atmosphere. For the activity of gold the particle size is essential. So for a good comparison we also tried to get small metal particles of about 3nm for the copper and silver catalysts. No literature data has been found for the preferential oxidation of CO on such small particles of copper and silver.

2.2 Experimental

2.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x) and Li_2O on alumina were prepared by pore volume impregnation of γ-Al_2O_3 (Engelhard) with the corresponding nitrates. After calcination at 350°C these oxides were used as support for the catalysts. The prepared mixed oxides have an intended Ce/Al and Li/Al ratio of 1/15. The copper and gold catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent [29]. An appropriate amount of $HAuCl_4$.3aq (99.999% Aldrich chemicals), $AgNO_3$ or $CuNO_3$.3aq was added to a suspension of purified water containing γ-Al_2O_3 or the mixed oxide. The intended M/Al ratio was 1/75 (M=Cu,Ag or Au). This ratio of 1:75 is equal to 0.53at% M and resulted in 5wt% for gold, 2.5wt% for silver and 1.5wt% for copper. The temperature was kept at 80 °C allowing urea (p.a., Acros) to decompose ensuring a slow increase of pH. When a pH of around 8-8.5 was reached the slurry was filtrated and washed thoroughly with water and dried overnight at 80 °C. Silver catalysts could not be prepared with urea, because a soluble $[Ag(NH_3)_2]^+$ complex is formed. So the silver catalysts were either prepared by homogeneous deposition precipitation using Na_2CO_3 as precipitating agent or by liquid phase reduction(LPR) using glucose as reducing agent. With the latter method it is possible to deposit metallic silver particles on the supporting oxide. The catalysts were thoroughly ground to ensure that the macroscopic particle size was around 200μm for all the catalysts used in this study. Prior to the activity measurement all catalysts were reduced at 400°C with hydrogen.

2.2.2 Catalyst characterization

The metal loading was verified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Varian Vista-MPX. For that purpose, a small fraction of the

catalyst was dissolved in diluted HNO_3 (copper and silver) or aqua regia (gold). X-ray diffraction measurements were done using a Philips Goniometer PW 1050/25 diffractometer equipped with a PW Cu 2103/00 X-ray tube operating at 50kV and 40mA. The average particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [30].

2.2.3 Activity measurements

Prior to activity experiments the catalysts were reduced with H_2 (4 vol% in He) at 400 °C for 2 hours. Activity tests of the catalysts were performed in a micro reactor system. The amount of catalyst used was 200mg for the Au/γ-Al_2O_3, Ag/γ-Al_2O_3 and Cu/γ-Al_2O_3 catalysts. When the catalyst contained CeO_x and/or Li_2O the amount of catalyst was adjusted in such a way that the amount of metal (Au, Ag or Cu) was similar for all the catalysts with and without additives. Gas mixtures (4vol% in helium) used were CO+O_2 (ratio 1), CO+O_2 +H_2 (ratio 1:1:5), CO+O_2 +H_2 (ratio 1:1:50) and CO+O_2 +H_2 (ratio 1:5:50). Typically a total gas flow of 40ml/min (GHSV $\approx$ 2500h^{-1}) was maintained. The effluent stream was analyzed on-line by a gas chromatograph (HP 8590) with a CTR1 column (Alltech) containing a porous polymer mixture and an activated molecular sieve. The experiments were carried out at a pressure of 1 bar. Each measurement consists of four temperature programmed cycles of heating and cooling, with a rate of 4°C/min. No deactivation of the catalysts was observed except for the Ag/γ-Al_2O_3 and Ag/Li_2O/γ-Al_2O_3 catalyst in CO oxidation in the absence of H_2. Unless otherwise stated the results of the second cooling stage are depicted in the figures.

2.2.4 FTIR measurements

Catalyst powder was pressed into a disc that was mounted in a vacuum cell (base pressure 5×10^{-6} mbar) and was reduced in situ by H_2 or oxidized by O_2 for 1h at 350 °C. Infrared spectra were recorded with a single-beam spectrometer (Mattson Galaxy 2020) operated at a resolution of 4cm^{-1}. To reduce the noise/signal ratio 128 scans were taken per spectrum and the applied infrared range was 3000-1000cm^{-1}. Background spectra were recorded before admitting reaction mixtures. Reactant gases used were O_2 (99.998%) , H_2 (99.999%) and CO (99.997%, Messer Griesheim), and were admitted up to a pressure between 1 and 100mbar. Finally the spectra were corrected for gas phase bands of CO and backgrounds were subtracted.

2.3 Results

2.3.1 Characterization

The average particle size of the fresh catalysts could not be determined by XRD because the size of the particles was apparently below 3nm. The results of the characterization of the catalysts after the reaction are shown in table 2.1. The catalysts without additives contain small particles of 3-4nm. When ceria and Li_2O are added the average particle size is lower than the detection limit (3nm) of the XRD machine. The particle size of the silver catalysts prepared with liquid phase reduction was about 8-9nm. The actual metal loading was almost equal to the intended metal loading. The XRD spectra after reaction (CO oxidation) of the all the silver catalysts prepared with HDP show that the silver particles are converted to Ag_2O. The XRD spectra of silver based catalysts prepared by LPR show only peaks of metallic silver after the reaction.

Table 2.1: Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Average particle size (nm)
Au/Al_2O_3	4.6±0.1	4.3±0.1
$Au/CeO_x/Al_2O_3$	4.1±0.1	<3.0
$Au/Li_2O/Al_2O_3$	4.5±0.3	3.2±0.1
$Au/CeO_x/Li_2O/Al_2O_3$	4.0±0.2	<3.0
Ag/Al_2O_3	2.3±0.1	4.5±0.1
$Ag/CeO_x/Al_2O_3$	1.7±0.1	3.3±0.1
$Ag/Li_2O/Al_2O_3$	2.2±0.1	<3.0
$Ag/CeO_x/Li_2O/Al_2O_3$	1.6±0.1	<3.0
Cu/Al_2O_3	1.5±0.1	3.5±0.1
$Cu/CeO_x/Al_2O_3$	1.0±0.1	<3.0
$Cu/Li_2O/Al_2O_3$	1.4±0.1	<3.0
$Cu/CeO_x/Li_2O/Al_2O_3$	1.0±0.1	<3.0
$Ag(LPR)/Al_2O_3$	2.5±0.1	9.2±0.2
$Ag(LPR)/CeO_x/Al_2O_3$	1.7±0.1	8.8±0.2
$Ag(LPR)/Li_2O/Al_2O_3$	2.4±0.1	8.7±0.2
$Ag(LPR)/CeO_x/Li_2O/Al_2O_3$	1.7±0.1	8.5±0.1

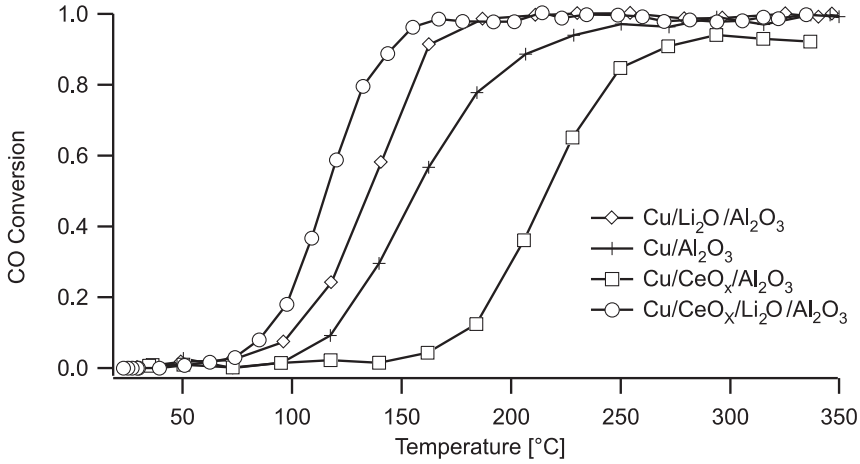

Figure 2.1: Effect of additives CeO_x and Li_2O on the CO conversion on copper based catalysts in the CO oxidation in the absence of H_2

2.3.2 CO oxidation in the absence of H_2

The behavior of the catalysts in CO oxidation with oxygen in a ratio of 1:1 in the absence of H_2 is illustrated in table 2.2 and in figures 2.1, 2.2, 2.3, 2.4. Gold is the most active catalyst followed by copper and silver. The combined addition of both Li_2O and CeO_x has a very beneficial effect on the activity of the copper and gold catalysts, whereas addition of only CeO_x has a negative effect and the addition of only Li_2O a small positive effect on the activity of the catalysts. Addition of Li_2O and/or Li_2O and CeO_x to the silver catalysts prepared by liquid phase reduction does not affect the catalyst performance, see figure 2.4. The silver catalysts prepared by homogeneous deposition precipitation show a different behavior as is depicted in figures 2.1, 2.2, 2.3. The silver only catalyst shows activity at a much lower temperature than the silver catalyst prepared by LPR, but deactivates already in the first heating stage above 250°C, in the following stages the deactivation continues. Addition of ceria stabilizes the silver catalyst but the $T_{50\%}$ is increased to 180°C. Li_2O addition shows a very small negative effect on these silver catalysts. The effect of addition of both oxides is comparable to addition of CeO_x only.

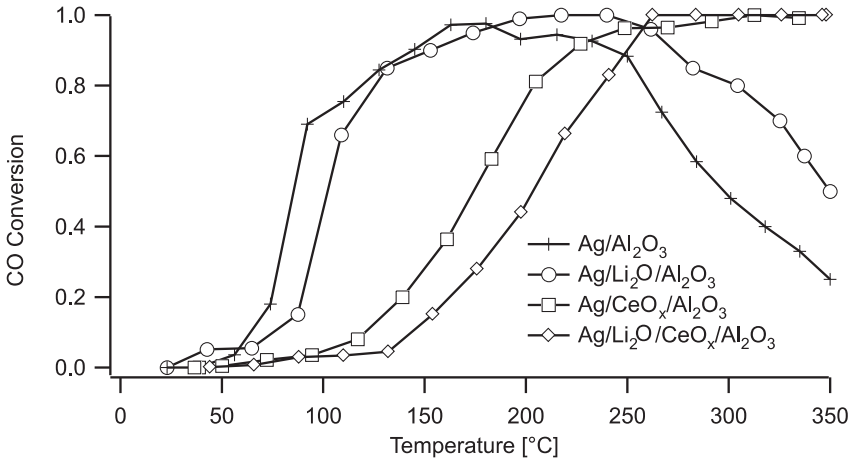

Figure 2.2: Effect of additives CeO_x and Li_2O on the CO conversion on silver based catalysts in the CO oxidation in the absence of H_2

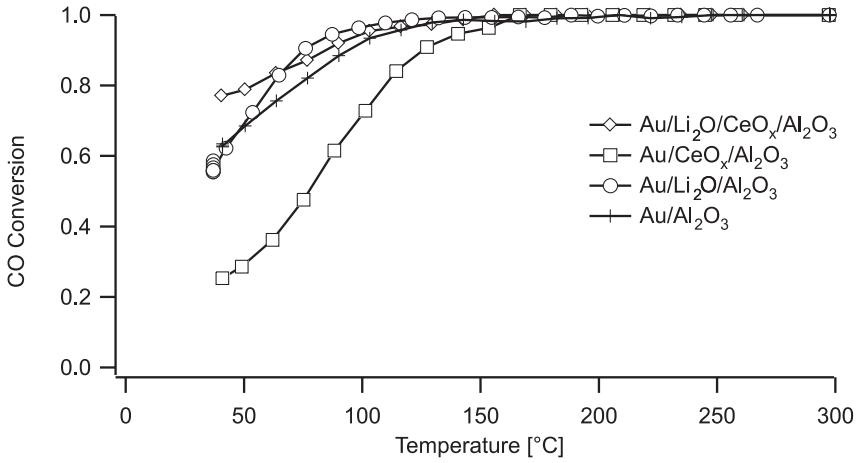

Figure 2.3: Effect of additives CeO_x and Li_2O on the CO conversion on gold based catalysts in the CO oxidation in the absence of H_2

Table 2.2: Effect of addition of oxides on the catalytic activity for the CO/O_2 reaction. Temperature of 50% conversion($T_{50\%}$) and temperature of 95% conversion($T_{95\%}$)

Catalyst	$T_{50\%}$ (°C)	$T_{95\%}$ (°C)
Au/Al_2O_3	50	100
$Au/CeO_x/Al_2O_3$	75	150
$Au/Li_2O/Al_2O_3$	50	100
$Au/CeO_x/Li_2O/Al_2O_3$	RT	100
Ag/Al_2O_3	80	160
$Ag/CeO_x/Al_2O_3$	180	250
$Ag/Li_2O/Al_2O_3$	100	185
$Ag/CeO_x/Li_2O/Al_2O_3$	200	250
Cu/Al_2O_3	160	210
$Cu/CeO_x/Al_2O_3$	210	250
$Cu/Li_2O/Al_2O_3$	140	190
$Cu/CeO_x/Li_2O/Al_2O_3$	110	150
$Ag(LPR)/Al_2O_3$	210	250
$Ag(LPR)/CeO_x/Al_2O_3$	200	250
$Ag(LPR)/Li_2O/Al_2O_3$	210	250
$Ag(LPR)/CeO_x/Li_2O/Al_2O_3$	200	250

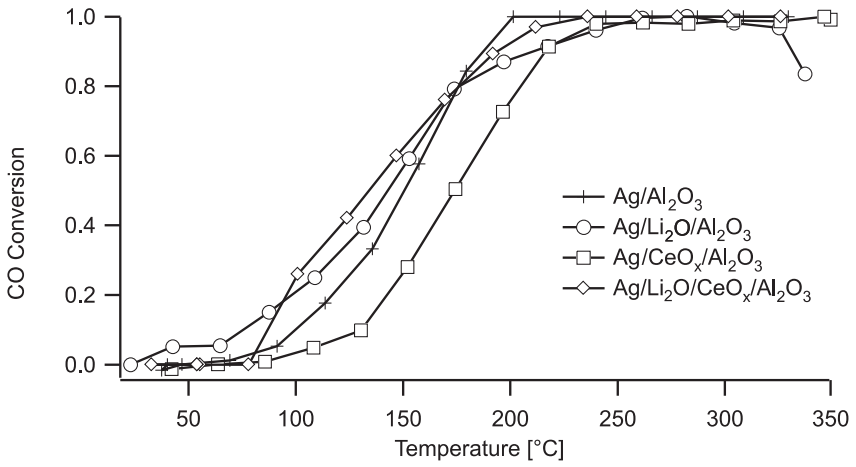

Figure 2.4: CO conversion over silver catalysts, prepared by liquid phase reduction

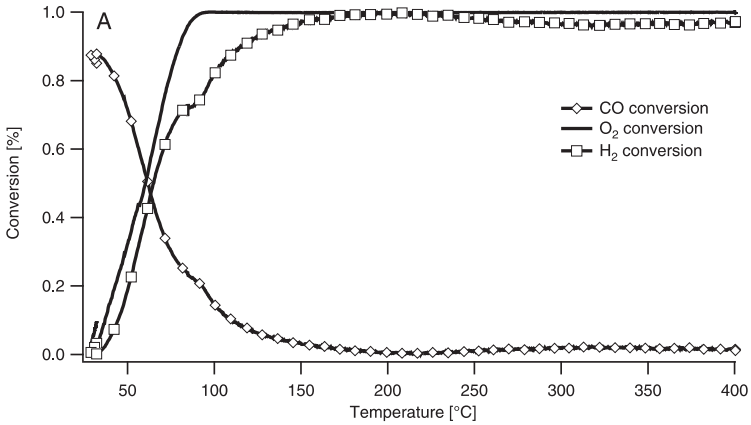

Figure 2.5: CO,O_2 and H_2 conversion over $M/Li_2O/CeO_x/\gamma\text{-}Al_2O_3$ catalysts M= Au(A), Ag(B) and Cu(C). H_2 conversion is normalized to theoretical maximum conversion. $CO/O_2/H_2$ =1:1:5

2.3.3 Preferential oxidation of CO in the presence of H_2 ($CO:O_2:H_2$ =1:1:5)

Figures 2.5, 2.6, 2.7 shows that when CeO_x and Li_2O are added to the Au, Ag, Cu based catalysts, the CO oxidation precedes the H_2 oxidation on all three metals when a ratio of $CO:O_2:H_2$ (1:1:5) is used. At temperatures below 100°C $Au/\gamma\text{-}Al_2O_3$ is the most active catalyst. It shows a maximum CO conversion at room temperature (RT) which decreases to 5% at 350°C as the H_2 conversion increases. The CO oxidation on silver starts at 150°C and reaches a maximum at 250°C, and the H_2 conversion starts at 275°C. On $Cu/\gamma\text{-}Al_2O_3$ the CO conversion exceeds the H_2 conversion by 125 degrees. The CO conversion starts at 75°C and the H_2 conversion at 200°C. Addition of CeO_x and/or Li_2O to the silver catalyst does not effect the performance of the catalyst (not shown). Addition of CeO_x to copper in the CO oxidation results in a decrease of CO conversion above 200°C shown in figure 2.8. Addition of Li_2O has a small beneficial effect on the CO conversion, and the combined addition of both Li_2O and CeO_x resulted in the best performing Cu-based catalyst, just like in the experiment in the absence of hydrogen presented in section 2.3.2.

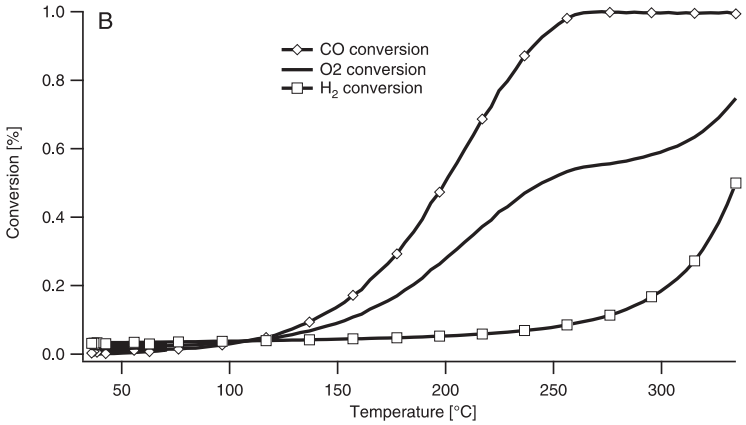

Figure 2.6: CO,O_2 and H_2 conversion over $M/Li_2O/CeO_x/\gamma\text{-}Al_2O_3$ catalysts M= Au(A), Ag(B) and Cu(C). H_2 conversion is normalized to theoretical maximum conversion. $CO/O_2/H_2$ =1:1:5

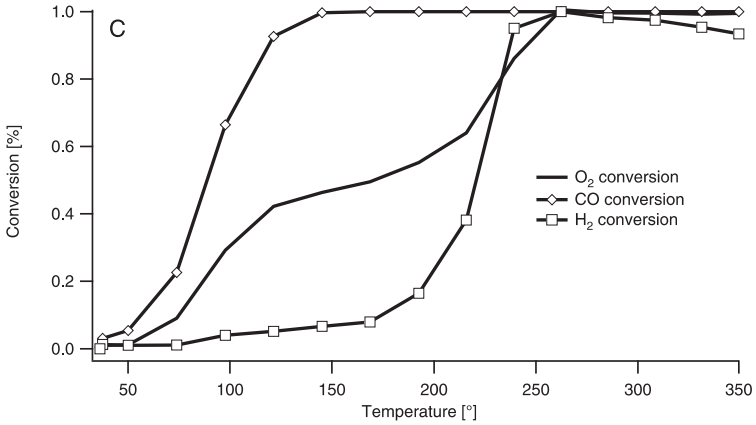

Figure 2.7: CO,O_2 and H_2 conversion over $M/Li_2O/CeO_x/\gamma\text{-}Al_2O_3$ catalysts M= Au(A), Ag(B) and Cu(C). H_2 conversion is normalized to theoretical maximum conversion. $CO/O_2/H_2$ =1:1:5

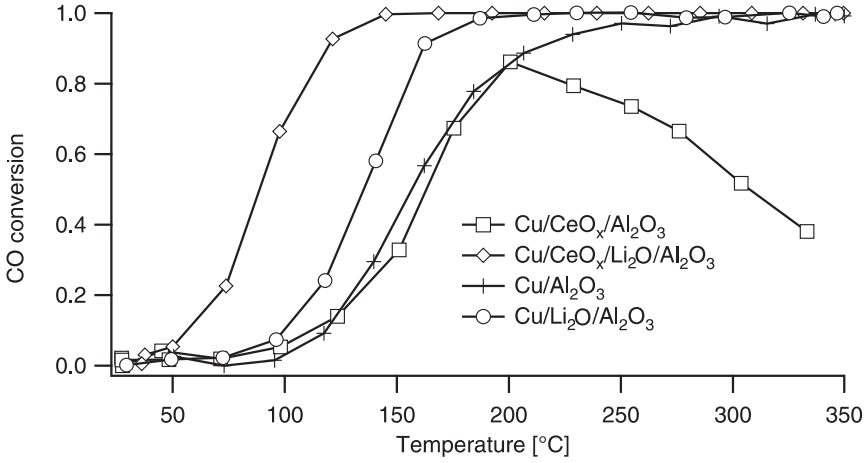

Figure 2.8: Effect of additives CeO_x and Li_2O on the CO conversion on Cu catalysts

2.3.4 Preferential CO oxidation in a hydrogen rich environment ($CO:O_2:H_2$ =1:1:50)

The results of CO oxidation in a hydrogen rich feed are presented in figure 2.9. The Cu/Al_2O_3 and the $Cu/Li_2O/Al_2O_3$ catalysts show a sharp maximum in CO conversion at 175°C. Addition of CeO_x improves the performance of the catalysts. The onset of CO conversion is lowered to 50°C. The catalyst with both Li_2O and CeO_x has the same activity as the catalyst with only ceria added. The silver catalyst shows poor performance in CO oxidation with a maximum CO conversion of 20% at 105°C. Addition of Li_2O shifts the temperature of maximum conversion to 90°C. Addition of CeO_x increases the maximum conversion to 40% at 130°C. Addition of both Li_2O and CeO_x shifts the temperature of maximum conversion to 110°C, compared to the catalyst with ceria. The gold catalysts show a maximum CO conversion at RT. The CO conversion decreases with increasing temperature to about 5% at 300°C. The silver and gold containing catalysts with addition of ceria show an increase of CO conversion above 250°C. This is due to the CeO_x/Al_2O_3 support, which shows a increasing conversion of CO at higher temperatures.

In an attempt to get maximum CO conversion we also performed measurements with more O_2 in the gas stream. The ratio used was $CO:O_2:H_2$ =1:5:50. The results

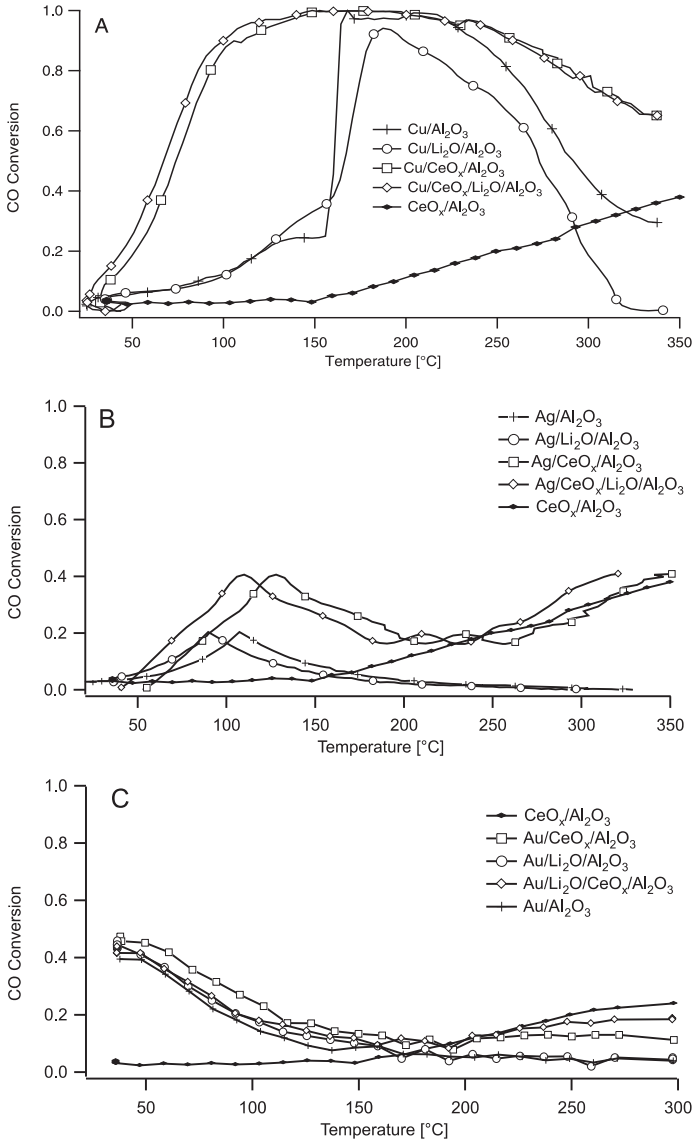

Figure 2.9: Effect of additives CeO_x and Li_2O on gold, silver and copper based catalysts in the CO conversion in a hydrogen rich environment. $CO/O_2/H_2$ =1:1:50

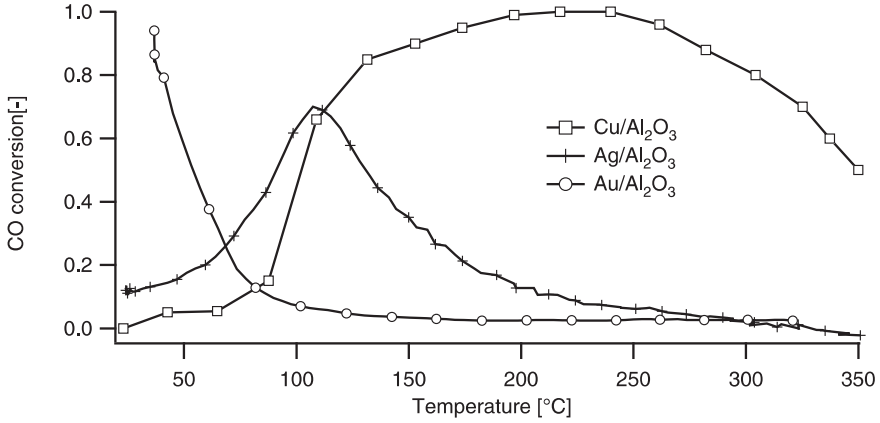

Figure 2.10: CO conversion in a hydrogen rich environment ($CO:O_2:H_2$ =1:5:50) over Cu/Al_2O_3, Ag/Al_2O_3 and Au/Al_2O_3

are presented in figure 2.10 and figure 2.11. Under these conditions maximum CO conversion can also be reached for the multicomponent gold and silver catalysts. For gold this was reached at RT and for silver at 95°C. The results of the copper catalyst were comparable to the results with less oxygen as shown in figure 2.9. Under these conditions the combined addition of Li_2O and CeO_x results in a wider temperature range at which CO is converted to CO_2.

2.3.5 FTIR

The effect of addition of Li_2O on the CO adsorption on the metal particles has been investigated with FTIR. The results are presented in figure 2.12. On Ag/Al_2O_3 and $Ag/Li_2O/Al_2O_3$ no CO absorption band was found at pressures up to 100mbar. A band at 2165cm^{-1} was found when the silver catalyst was oxidized at 300°C with oxygen. This band can be assigned to CO on oxidic silver [31]. Addition of Li_2O to the copper catalysts shifts the CO absorption band from 2125cm^{-1} to 2106cm^{-1}. On the gold catalyst there is a shift from 2113cm^{-1} to 2104cm^{-1}. Besides the frequency shift the absorption bands become narrower and more symmetrical. The frequency of the CO absorption bands on gold and copper can be assigned to CO adsorbed on metallic particles [13].

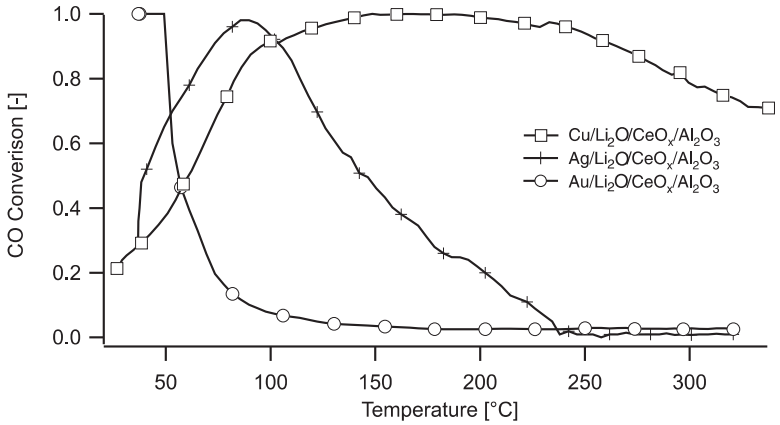

Figure 2.11: CO conversion in a hydrogen rich environment over $M/CeO_x/Li_2O/Al_2O_3$ M= Au, Ag, Cu ($CO:O_2:H_2$ =1:5:50)

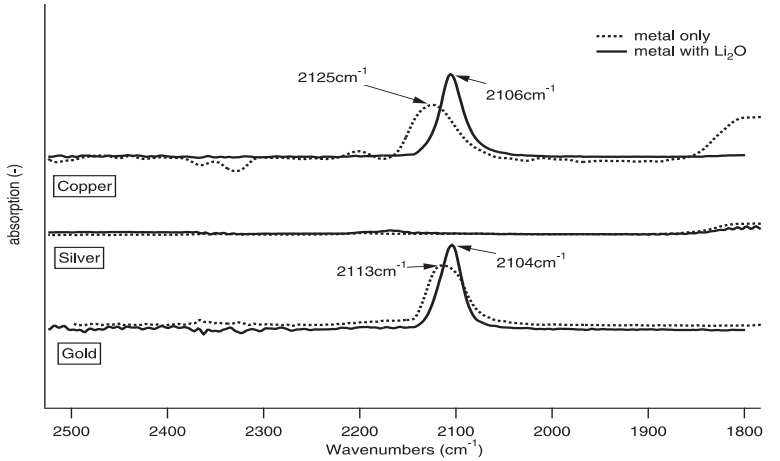

Figure 2.12: Effect of addition of Li_2O on the CO absorption band for copper, silver and gold based catalysts at RT. CO pressure is 30mbar for copper and gold. CO pressure for silver based catalysts is 100mbar

2.4 Discussion

2.4.1 Particle size

The catalytic activity of gold is very dependent on the gold particle size [11]. In this paper it is shown that also copper and silver, when deposited as nano particles on γ-Al_2O_3 are active in low-temperature CO oxidation. In an attempt to prepare catalysts with small metallic silver particles two preparation methods were used. With LPR it is possible to directly deposit metallic silver on the support [31] and using HDP with Na_2CO_3 as precipitating agent small silver particles can be deposited, but these particles have to be reduced to become metallic. These silver catalysts show different behavior. The silver catalysts prepared by LPR show activity at 200°C whereas the silver catalysts prepared by homogeneous deposition precipitation already show activity at 100°C. These two catalysts differ in the particle size of the silver particles. The catalyst prepared by LPR contains big particles of about 8-9nm, compared to silver particles of $<$3nm for the silver catalysts prepared by HDP. The catalyst with the smaller particles is the most active one. However the metallic silver particles smaller than 3nm are not stable in an oxidizing environment, whereas the bigger silver particles of 8-9nm are stable. Addition of CeO_x or Li_2O to the silver catalysts results in an increase in CO conversion for the small silver particles and has no effect for the bigger silver particles. This suggests that the chemistry on these catalysts may be different. Probably CO adsorbed on 8-9nm silver particles combines with O_{ad} on large metallic silver particles to CO_2 in a Langmuir-Hinshelwood type mechanism. This will explain why addition of CeO_x and Li_2O does not have any effect on the activity. The influence of addition of CeO_x and Li_2O to the $<$3nm silver particles suggests a different mechanism for the CO oxidation. It is proposed that the CO oxidation on silver is analogues to a mechanism for gold in the presence of transition metal oxides [16]. The CO binds onto the silver and reacts on the interface of the silver with oxygen supplied by the cerium oxide support. CeO_x also stabilizes the small silver particles.

2.4.2 Selective CO oxidation

The results presented in figures 2.5, 2.6, 2.7 show that Au/γ-Al_2O_3, Ag/γ-Al_2O_3 and Cu/γ-Al_2O_3 oxidize CO at lower temperatures than hydrogen. On silver and copper based catalysts maximum CO conversion is maintained at higher temperatures whereas on Au/γ-Al_2O_3 the start of hydrogen oxidation at 50°C lowers the CO conversion to 0 at 150°C. The copper catalysts are able to oxidize CO even if the hydro-

gen content is increased. Only at temperatures above 200°C there is a slight decrease in CO conversion. For silver and gold maximum conversion can only be reached at higher oxygen content. Gold is the most active catalyst at low temperature. But the optimal conversion of CO is probably at temperatures lower than was used in this study. Silver shows little activity in preferential CO oxidation with a maximum conversion of 40% if CeO_x and Li_2O are added. Probably the concentration of adsorbed CO on silver is too low.

2.4.3 Addition of Li_2O

Addition of Li_2O has a small positive effect on the activity of the copper and gold catalyst and the silver catalyst prepared by HDP in preferential CO oxidation. Figure 2.12 shows that addition of Li_2O to the catalysts results in a shift of the CO absorption band to lower wave numbers, which implies a stronger adsorption of the CO on the metal particles. The more symmetrical shape of the CO band suggests that the Li_2O has an effect on the morphology of the nanoparticles. These results are in agreement with Gluhoi et al. [26, 27] that Li_2O can act as a structural promoter. The absence of CO adsorption on a reduced silver catalyst suggests a very low CO coverage at room temperature. This is in line with literature data [31] and suggests that the silver particles are in the metallic state after reduction. Apparently, the presence of Li_2O does not result in a sufficient increase in CO coverage.

2.4.4 Addition of CeO_x

Ceria has only on the gold catalysts a positive effect on the CO conversion. Addition of CeO_x to the silver catalysts with $<$3nm particles stabilizes the silver particles, but increases the $T_{50\%}$ to 180°C. Addition of CeO_x to the copper catalyst also has a negative effect in the CO oxidation with a small amount of H_2 present. Figure 2.8 shows that the CO conversion drops above 200°C. This is also reported by Avgouropoulos on a CuO-CeO_x catalyst [20]. With a large amount of hydrogen present CeO_x has a positive effect on the CO conversion on all three metals. Clearly, the CeO_x has an important role in the catalysis of the selective CO oxidation especially on copper. The proposed role is that CeO_x under strongly reducing conditions can provide the oxygen for the oxidation of CO to CO_2, but can also facilitate the oxidation of the silver and copper particles in a more oxidative environment.

2.4.5 Addition of CeO_x and Li_2O

Addition of both oxides provides the best performing catalysts under all conditions. The positive effect of addition of both oxides is greater than the contribution of both oxides separately. This synergistic effect has been reported before [28] but it is not completely understood. Probably the Li_2O prevents the oxidation of the metal particles under oxidizing conditions and stabilizes them, while CeO_x addition may result in another route of O supply needed for CO oxidation.

2.5 Conclusions

This study shows that all three IB metals are active in low temperature preferential CO oxidation provided that the metal particles are small (<3nm). Measurements showed that when the particle size of the silver is increased the CO oxidation is not affected by the additives and the CO oxidation is probably a reaction of adsorbed CO and O on the metal particle. CeO_x positively contributes to the gold catalyst in increasing its performance by supplying oxygen [32]. On silver and copper it has a negative effect. The role of Li_2O can be attributed to strengthening of the CO adsorption and stabilizing the small metallic particles. Addition of both CeO_x and Li_2O provides the best performing catalysts in selective CO oxidation. All three metals preferentially oxidize CO over H_2 at low temperatures in agreement with the DFT study of Kandoi [23]. Gold is the most active catalyst in CO oxidation with hydrogen present at low temperatures. Copper shows the highest selectivity toward CO at temperatures above 100°C and silver is the least active metal with low CO selectivity and activity. The $Cu/CeO_x/Li_2O/Al_2O_3$ shows the best activity in the selective oxidation in the temperature range in which the PEMFC is operating (100°C).

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3

A comparative study of the selective oxidation of NH_3 to N_2 over gold, silver and copper catalysts and the effect of addition of Li_2O and CeO_x

This paper describes the selective oxidation of ammonia into nitrogen over copper, silver and gold catalysts between room temperature and 400°C using different NH_3/O_2 ratios. The effect of addition of CeO_x and Li_2O on the activity and selectivity is also discussed. The results show that copper and silver are very active and selective toward N_2. However the multicomponent catalysts: $M/Li_2O/CeO_x/Al_2O_3$ (M:Au,Ag,Cu) perform the best. On all three metal containing catalysts the activity and selectivity is influenced by the particle size and the interaction between metal particles and support.

3.1 Introduction

The catalytic oxidation of ammonia is an important heterogeneous catalytic process and subject of many studies. The oxidation of ammonia can proceed via the following three principal reactions:

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \tag{3.1}$$

$$4\,NH_3 + 4\,O_2 \rightarrow 2\,N_2O + 6\,H_2O \tag{3.2}$$

$$4\,NH_3 + 3\,O_2 \rightarrow 2\,N_2 + 6\,H_2O \tag{3.3}$$

Reaction (3.1) is the first step in the so-called Ostwald process, where the formed NO reacts with O_2 to form NO_2. The nitric acid produced in this way is used for the production of, among others, fertilizers. For this process high temperatures (800-900°C) are required and a Pt/Rh gauze is used as catalyst. The N_2O which is formed in reaction (3.2) can be used as a precursor of atomic oxygen and may, therefore, potentially be used as selective oxidant of hydrocarbons [1, 2]. Therefore, there is recent interest in development of catalysts which convert NH_3 into N_2O with high selectivity. The process described in reaction (3.3) is potentially an efficient and simple method to abate ammonia pollution. It also may be used for the small scale production of pure nitrogen as a safety gas. In literature, many papers dealing with this reaction over various kinds of noble metal and metal oxide catalysts can be found. The earlier work has been reviewed by Il'Chenko et al. [3]. In more recent years various unsupported and supported catalysts have been extensively studied [4–7] for the selective oxidation of ammonia. A variety of metals including Ni, Mn, Fe, Cu, Pt, Ru and Ag supported on γ-Al_2O_3 have been tested mainly in the temperature range 200-600°C. The maximum N_2 selectivity obtained, ranges between 82 and 98%. Copper catalysts are very selective to nitrogen [5] but only at elevated temperatures, while silver catalysts convert ammonia already at temperatures below 200°C [4], but do not have a high selectivity to nitrogen.

In this study we prepared catalysts based on gold, silver and copper nano-particles on γ-Al_2O_3. In addition, the effect of adding Li_2O and CeO_x has been investigated. CeO_x is an active oxide for the oxidation of CO to CO_2. Previously reported results show that ceria has a promoting effect on the activity of the Au/Al_2O_3 catalyst in CO oxidation [8–10]. It was argued that the active oxygen was supplied by the ceria, rather than from the gasphase. Moreover it was reported that the size of the ceria

particles has a great influence on the activity of the catalyst [11]. A detailed study of Gluhoi et al. [12, 13] on the effects of addition of (earth) alkali metals to a Au/Al_2O_3 catalyst revealed that the main role of the (earth) alkali metals is that of a structural promoter. It stabilizes the gold particles. It was also found that the combination CeO_x + Li_2O acts as a very efficient promoter for Au based catalyts in many reactions, such as oxidation of hydrocarbons, CO and NH_3 [12,14,15] or reduction of NO by H_2 [16]. Comparable results have been found for copper and silver based catalysts [17]. The results of the gold catalysts in NH_3 oxidation have already been published in other papers of our group [12, 14, 15].

3.2 Experimental

3.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x) and/or Li_2O with alumina were prepared by pore volume impregnation of γ-Al_2O_3 (Engelhard) with the corresponding nitrates. After calcination at 350°C these oxides were used as supports for the Au, Cu or Ag based catalysts. The prepared mixed oxides have an intended atomic ratio Ce/Al and Li/Al of 1/15. The copper, silver and gold catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent [18]. An appropriate amount of $HAuCl_4$.3aq (99.999% Aldrich chemicals) or $CuNO_3$.3aq was added to a suspension of purified water containing γ-Al_2O_3 or the mixed oxide. The intended M/Al atomic ratio was 1/75 (M=Cu, Ag or Au). This ratio of 1:75 is equal to 0.53at% M and resulted in 5wt% for gold, 2.5wt% for silver and 1.5wt% for copper. The temperature was kept at 80 °C allowing urea (p.a.,Acros) to decompose ensuring a slow increase of pH. When a pH of around 8-8.5 was reached the slurry was filtrated and washed thoroughly with water and dried overnight at 80 °C. Because urea and silver atoms can form a soluble $Ag[NH_3]_2{}^+$ complex a large surplus of silver was needed to deposit enough silver on the Al_2O_3. The catalysts were thoroughly ground to ensure that the macroscopic particle size was around 200μm for all the catalysts used in this study. Prior to the activity measurement all catalysts were reduced at 400°C with hydrogen for 2 hours.

3.2.2 Catalyst characterization

The metal loading was verified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Varian Vista-MPX. For that purpose a small fraction of the catalyst was dissolved in diluted aqua regia. X-ray diffraction measurements were done using a Philips Goniometer PW 1050/25 diffractometer equipped with a PW Cu 2103/00 X-ray tube operating at 50kV and 40mA. The average particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [19].

3.2.3 Activity measurements

Activity tests of the catalysts were performed in a micro reactor system. The amount of catalyst used was 200mg for the Au/γ-Al_2O_3, Ag/γ-Al_2O_3 and Cu/γ-Al_2O_3 catalysts. When the catalyst contained CeO_x and/or Li_2O the amount of catalyst was adjusted in such a way that the amount of metal atoms (Au, Ag or Cu) was similar for all the catalysts with and without additives. Four different gas mixtures of NH_3 and oxygen were used. Both gases were 4vol% balanced in argon. The different NH_3:O_2 ratios used were 1:1, 1:5, 1:10 and 1:25. Typically a total gas flow of 40ml/min (GHSV $\approx$ 2500h^{-1}) was maintained. The effluent stream was analyzed on-line by a quadrupole mass spectrometer(Balzers). The experiments were carried out at a pressure of 1 bar. Each measurement consists of at least four temperature programmed cycles of heating and cooling, with a rate of 4°C/min. Unless otherwise stated the results of the second cooling stage are depicted in the figures. The only hydrogen containing product that was detected was water.

3.3 Results

3.3.1 Characterization

The average particle size of the fresh catalysts could not be determined by XRD because the size of the particles was below the detection limit of the XRD (3nm). The results of the characterization of the catalysts after the reaction are shown in table 3.1. The catalysts without additives contain small particles of 3-4nm. With ceria and Li_2O added the average particle size is lower than the detection limit (3nm). HRTEM data of comparable catalysts have been published in earlier papers of our

group [12, 13, 20]. The actual metal loading was almost equal to the intended metal loading. In addition, we have checked the catalysts for the Li and Ce contents with ICP-OES. These measurements showed that the appropriate amount of Li and/or Ce was deposited on the catalysts.

Table 3.1: Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Metal loading (at%)	Average particle size (nm)
Au/Al_2O_3	4.8±0.1	0.51	4.5±0.1
$Au/CeO_x/Al_2O_3$	4.0±0.2	0.42	3.3±0.3
$Au/Li_2O/Al_2O_3$	4.5±0.3	0.48	<3.0
$Au/CeO_x/Li_2O/Al_2O_3$	4.0±0.2	0.42	<3.0
Ag/Al_2O_3	2.2±0.1	0.47	4.9±0.2
$Ag/CeO_x/Al_2O_3$	1.8±0.1	0.39	3.9±0.2
$Ag/Li_2O/Al_2O_3$	2.2±0.1	0.47	<3.0
$Ag/CeO_x/Li_2O/Al_2O_3$	1.6±0.1	0.34	<3.0
Cu/Al_2O_3	1.3±0.1	0.46	3.6±0.3
$Cu/CeO_x/Al_2O_3$	1.0±0.1	0.35	<3.0
$Cu/Li_2O/Al_2O_3$	1.4±0.1	0.49	<3.0
$Cu/CeO_x/Li_2O/Al_2O_3$	1.0±0.1	0.35	<3.0

3.3.2 Copper catalysts

The used supports Al_2O_3, Li_2O/Al_2O_3, CeO_x/Al_2O_3 and $Li_2O/CeO_x/Al_2O_3$ without noble metal are inactive for the selective oxidation of ammonia at temperatures below 400°C. The results of the ammonia oxidation over copper catalysts with three different NH_3:O_2 ratios are presented in figure 3.1 and 3.2. In agreement with literature [5] the selectivity to N_2 on these copper catalyst is very high, almost 100%. The NH_3 conversion starts at 300°C with a NH_3:O_2 ratio of 1:1. When the O_2:NH_3 ratio is increased to 5, the temperature onset is not changed but full conversion is already reached at 350°C. When the oxygen content is further increased to a ratio of NH_3:O_2 = 1:25 the onset temperature is lowered to 200°C and the temperature of maximum conversion to 300°C. The results of addition of ceria and Li_2O are depicted in figure 3.3. Addition of Li_2O results is a small improvement of the performance of the Cu/Al_2O_3 catalyst. Addition of CeO_x has a more pronounced effect. The temper-

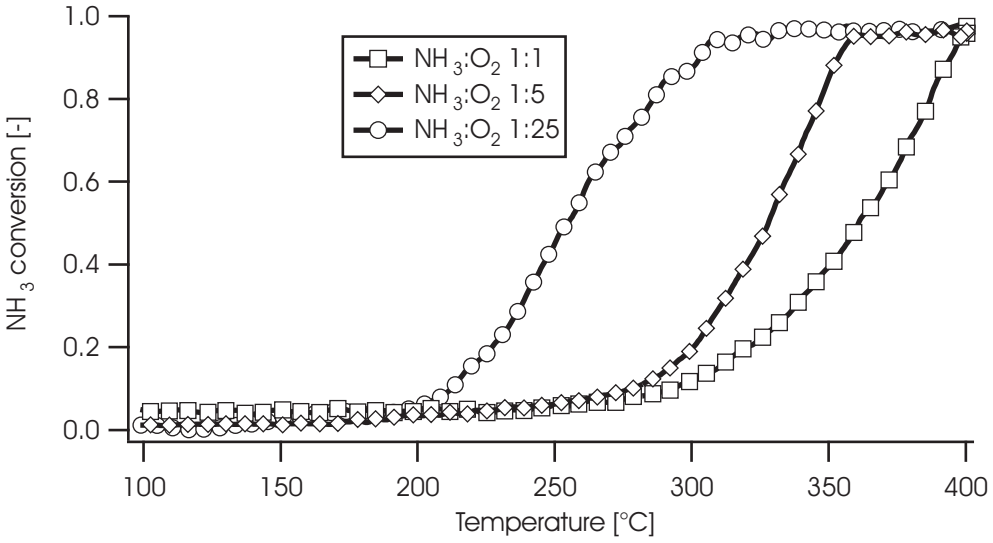

Figure 3.1: NH_3 conversion on Cu/Al_2O_3 catalyst for different NH_3:O_2 ratios.

ature onset of NH_3 conversion is lowered from 300°C towards 225°C. If also Li_2O is added to the $Cu/CeO_x/Al_2O_3$ catalyst again a small improvement is observed in the activity of the catalyst. Figure 3.4 shows the selectivity of the $Cu/Li_2O/CeO_x/Al_2O_3$ catalyst with a NH_3:O_2 ratio of 1:1. Only at temperatures below 200-250°C some N_2O is formed. Above that temperature only N_2 is formed.

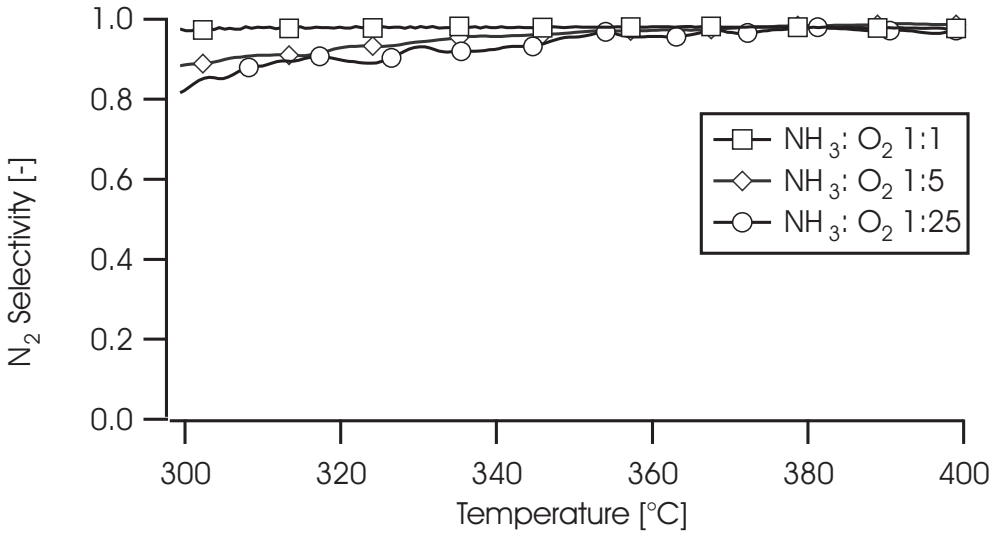

Figure 3.2: N_2 selectivity of the Cu/Al_2O_3 catalyst for different NH_3:O_2 ratios.

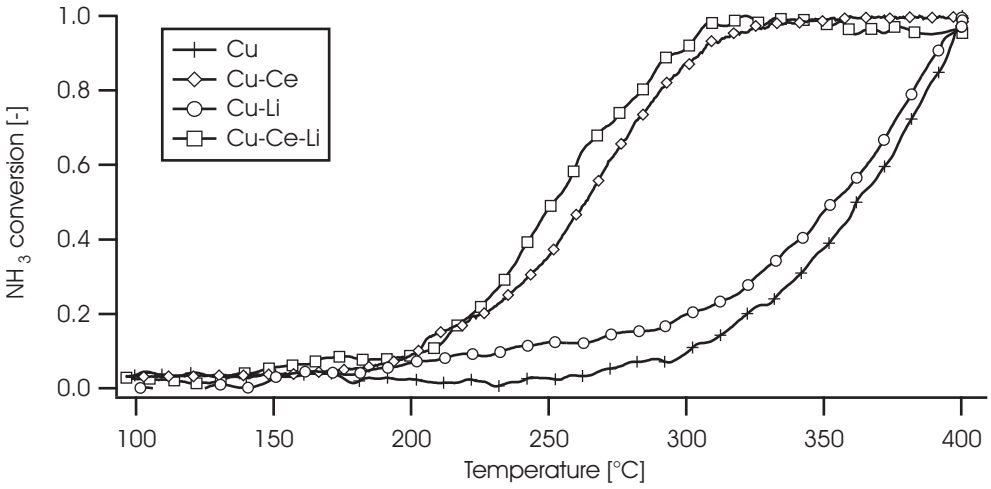

Figure 3.3: Effect of addition of Li_2O, CeO_x and Li_2O + CeO_x on the NH_3 conversion over Cu/Al_2O_3 catalysts, NH_3:O_2 = 1.

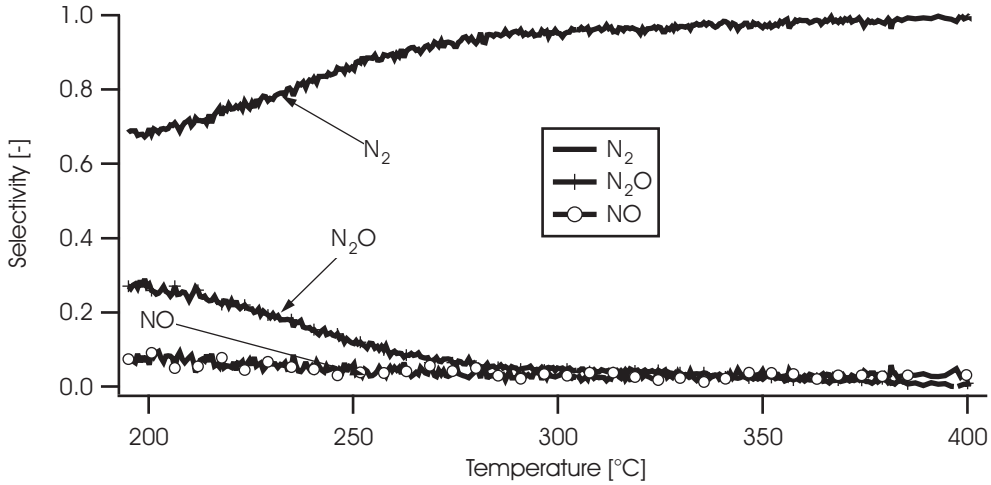

Figure 3.4: Selectivity of the $Cu/Li_2O/CeO_x/Al_2O_3$ catalyst, NH_3:O_2 =1.

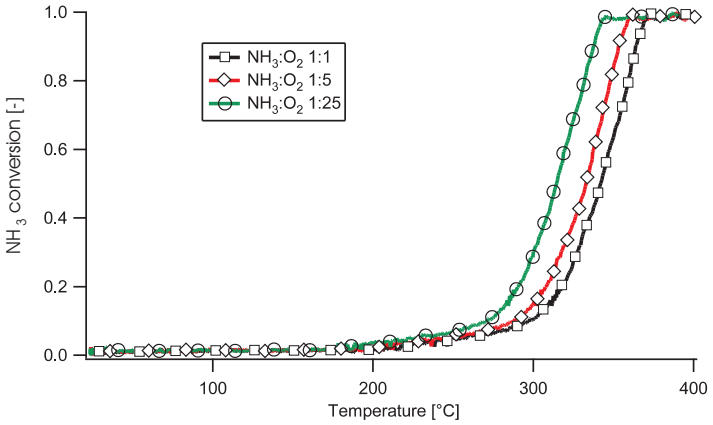

Figure 3.5: NH_3 conversion of Ag/Al_2O_3 catalyst for different NH_3:O_2 ratios.

3.3.3 Silver Catalysts

The NH_3 conversion over the Ag/Al_2O_3 catalysts is shown in figure 3.5. At a NH_3/O_2 ratio of 1, the onset temperature of NH_3 conversion is 300°C. Increasing the O_2/NH_3 ratio results in only a slightly lower onset temperature. In the temperature region of 300 - 400°C mainly N_2 is formed as can be seen in figure 3.6. With the NH_3/O_2 ratios of 1:1 and 1:5 the selectivity starts from 90% at 300°C and increases to 100% at 400°C. When the amount of oxygen is further increased to a ratio of NH_3:O_2 = 1:25 the selectivity at 300°C is increased to 98%. At temperatures above 360°C the selectivity drops towards 80%. In this temperature region some N_2O is formed. The results of addition of CeO_x and Li_2O are shown in figure 3.7. Similar to the copper catalysts, addition of Li_2O has a very small effect on the activity of the Ag based catalyst, while the selectivity was not affected by addition of Li_2O. Addition of CeO_x results in a shift of the onset temperature from 300°C to 200°C. Again no effect on the selectivity is detected. When Li_2O is added to the $Ag/CeO_x/Al_2O_3$ catalyst a further improvement on the activity is obtained. The onset temperature remains about 200°C. The temperature where the conversion reaches maximum is decreased from 340°C to 260°C. The selectivity of this catalyst is shown in figure 3.8. Below 300°C small amounts of NO and N_2O are formed, but the main product is N_2. The selectivity increases with increasing temperature and reaches 100% at 300°C.

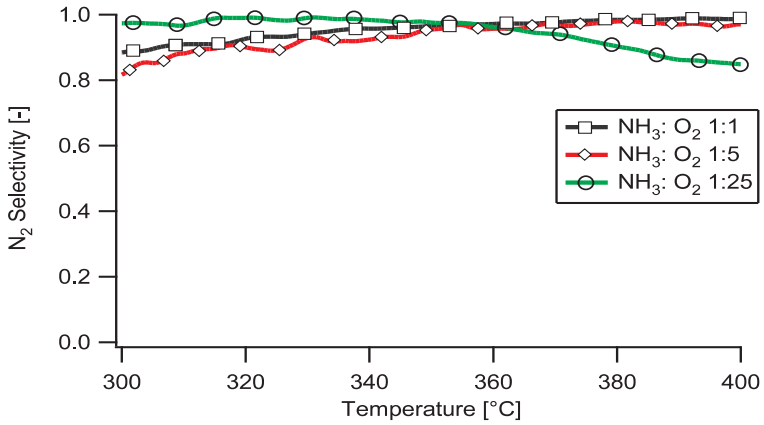

Figure 3.6: N_2 selectivity on the Ag/Al_2O_3 catalyst for different NH_3:O_2 ratios.

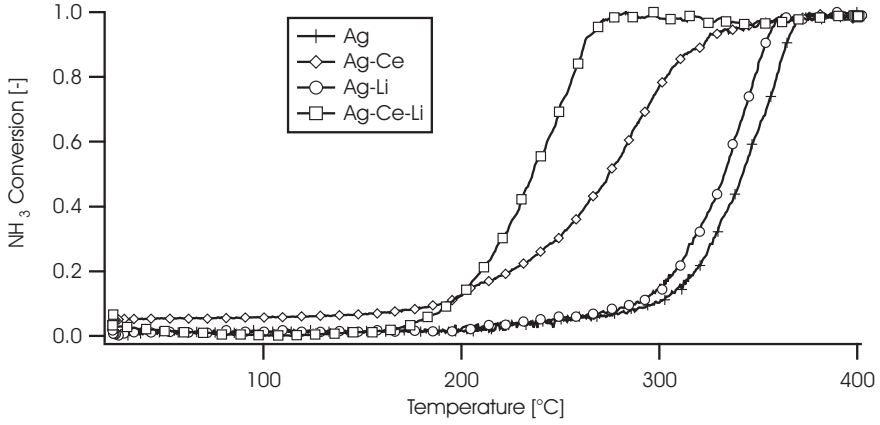

Figure 3.7: Effect of addition of Li_2O, CeO_x and Li_2O + CeO_x on the NH_3 conversion of Ag/Al_2O_3 catalysts, NH_3:O_2 = 1.

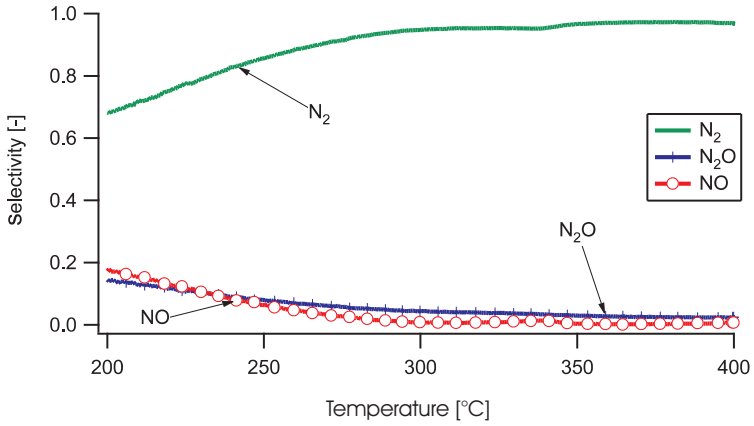

Figure 3.8: Selectivity of the $Ag/Li_2O/CeO_x/Al_2O_3$ catalyst, NH_3:O_2 = 1.

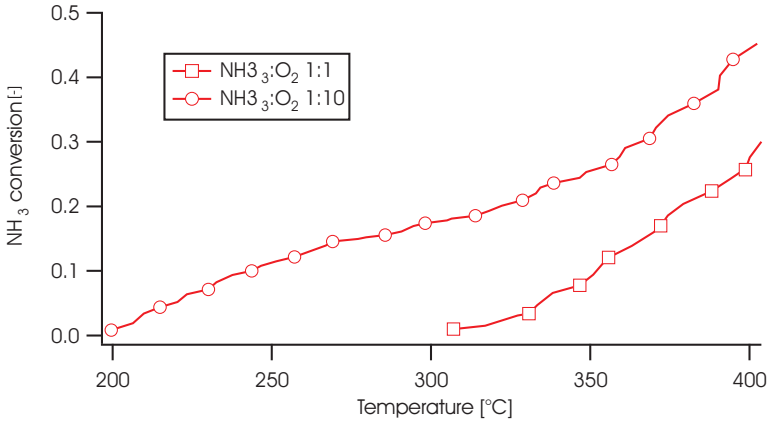

Figure 3.9: NH_3 conversion of Au/Al_2O_3 catalyst for different NH_3:O_2 ratios [12].

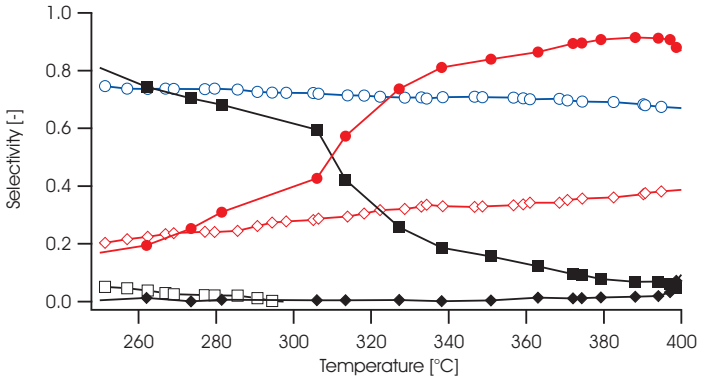

Figure 3.10: Product distribution vs temperature during NH_3 oxidation over Au/Al_2O_3 for two different reactant ratios. Full symbols: NH_3:O_2 = 1:1, open symbols: NH_3:O_2 = 1:10. Selectivity to N_2O(♦), Selectivity to N_2 (●), Selectivity to NO(■) [12].

3.3.4 Gold Catalysts

Figure 3.9 and 3.10 show that over gold based catalysts, at a NH_3/O_2 ratio of 1 a maximum conversion of 30% is obtained at 400°C with a selectivity to N_2 above 80%. The NH_3 conversion increases with increasing O_2 in the feed. For a O_2/NH_3 ratio of 10 the onset temperature is 200°C and a conversion of 45% is reached at 400°C. At 200°C the selectivity towards N_2 is about 78% and slowly decreases to 65% as the temperature is increased to 400°C. This decrease in N_2 selectivity is due to an increase in the N_2O selectivity. Figure 3.11 compares the catalytic activity of the gold based catalysts when the promoters are also present. Clearly the $Au/CeO_x/Li_2O/Al_2O_3$ catalyst showed the best activity [12]. The catalyst is already active at 230°C. In contrast to the copper and silver catalysts the addition of Li_2O to the Au/Al_2O_3 and $Au/CeO_x/Al_2O_3$ catalysts results in a large improvement of the activity. If figure 3.12 is compared to figure 3.10 it can be seen that the addition of ceria has a significant effect on the selectivity. At temperatures below 280°C mainly N_2 is formed. At higher temperatures the main product becomes N_2O. The $Au/CeO_x/Li_2O/Al_2O_3$ catalyst shows an increase in N_2 selectivity at the expense of selectivity to N_2O above 380°C. If also Li_2O is added no increase of N_2 production, in this temperature region, is observed.

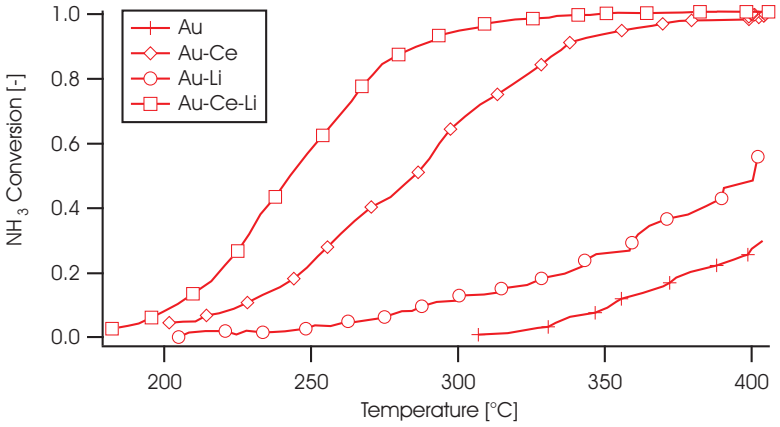

Figure 3.11: Effect of addition of Li_2O, CeO_x and Li_2O + CeO_x on the NH_3 conversion of Au/Al_2O_3 catalysts [12].

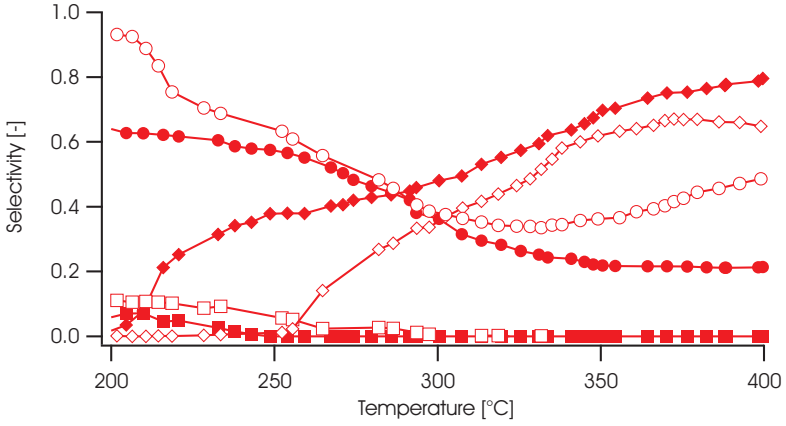

Figure 3.12: Product distribution vs temperature during NH_3 oxidation over $Au/CeO_x/Al_2O_3$ (full symbols) and $Au/Li_2O/CeO_x/Al_2O_3$ (open symbols): Selectivity to N_2O(♦), Selectivity to N_2 (●), Selectivity to NO(■) [12].

3.4 Discussion

3.4.1 Copper catalyst

An extensive study concerning ammonia oxidation on Cu/Al_2O_3 catalyst was reported by Friedman et al. [21] in 1978. Together with the results of another group [22] the authors came to the conclusion that at low copper loadings and calcination temperatures below 500°C the copper mainly exists as surface spinels ($CuAl_2O_4$). This was confirmed by results of Gang et al. [5,23]. They could not detect copper particles with HRTEM on catalysts with loadings of 10% or lower. With higher loading CuO particles were detected. Because the catalysts with lower loading were more active they concluded that the $CuAl_2O_4$ particles were more active than the CuO phase. Based on TPD measurements they also concluded that both surface and lattice oxygen can react with NH_3 to produce N_2. They stated that the first mentioned O-species was the most active one. Increasing the O_2/NH_3 ratio does increase the conversion but decreases the selectivity to N_2. Using a different preparation method and reduction in hydrogen instead of calcination in air we were able to produce small metallic copper particles at low loadings before reaction. These metallic particles are readily oxidized to copper oxide especially in oxygen rich reaction mixtures. The 1.5wt% Cu/Al_2O_3 catalyst showed a similar activity as the 5wt% catalyst of Gang et al. [5] and almost 100% selectivity to N_2. In agreement with that study increasing the O_2/NH_3 ratio enhanced the conversion. If CeO_x is added a great improvement in activity is obtained without loss in selectivity to N_2. This improvement can be explained by giving ceria a role as cocatalyst which consists in providing active oxygen to the active copper species. In the preparation of the catalyst the cerium oxide was deposited first and the copper was deposited afterwards. In this case it is not likely that surface spinels ($CuAl_2O_4$) were formed. CuO-CeO species may be formed but according to [24] those species are only active above 300°C in ammonia oxidation. Therefore, it is not likely that these species cause the improved actvitity of the $Cu/CeO_x/Al_2O_3$ catalyst. Possibly the reaction takes place at the interface of the copper nanoparticles and the ceria.

3.4.2 Silver catalysts

The activity of silver in the selective oxidation of ammonia has been previously studied by Gang et al. [4,23]. They compared silver powder with Ag/SiO_2 and Ag/Al_2O_3. The silver powder was very active, similar to Ag/SiO_2. These catalysts were superior to noble metal catalysts, such as Pt and Ir at temperatures below 200°C, but were

not very selective at low temperatures and reached a maximum selectivity to N_2 of around 75% at 300°C. The Ag/Al_2O_3 catalyst showed a better selectivity of around 80% to N_2 at low temperatures. At temperatures above 300°C the selectivity dropped due to the large NO production. They suggested a mechanism which consisted of two steps. The first one is a fast oxidation of NH_3 to NO on the silver particles. The second step is a reduction of the NO to N_2 or N_2O. They suggested that the second step was enhanced by the interaction between silver and the alumina, resulting in an improved selectivity to N_2. The possible effect of the difference in particle size of the Ag/Al_2O_3 (8nm) and Ag/SiO_2(24nm) catalyst has not been discussed in that paper. The silver catalysts we studied have a smaller Ag particle size (table 3.1). With these smaller particles no activity was found below 250°C. With all three O_2/NH_3 ratios the conversion is similar. It is well known that atomically adsorbed oxygen desorbs at around 280°C from a silver surface [25]. Possibly the ammonia oxidation is hindered by these atomically adsorbed oxygen. In the temperature region that the silver catalyst is active in NH_3 oxidation a very high selectivity towards N_2 is obtained. The chemical behavior is very different from the catalysts studied by Gang et al. [23]. Besides the differences in activity they found a large effect of the O_2/NH_3 ratio. It might be that the mechanism on the very small silver particles is different. Li_2O can act as a structural promoter [13, 16, 17]. It stabilizes the small silver particles which results in smaller particles (table 3.1). As addition of Li_2O shows only a small effect on the activity and no effect on the selectivity, it is unlikely that Li_2O influences the reaction chemistry. Addition of CeO_x or the combination of CeO_x and Li_2O does greatly influence the activity but not the selectivity. As the oxygen storage capability in oxidation reactions of ceria is well known, it is possible that the promoting role of CeO_x is related to an improved supply of active oxygen to the silver particles. Clearly, as Gang et al. [4] stated, the interaction between silver and the support has a great influence on the ammonia oxidation. But also the particle size should be taken into account. The smaller the particles the higher the selectivity to N_2. This suggests a model in which the reactions at the interface of silver with the ceria support is very important for high selectivity to nitrogen.

3.4.3 Gold Catalysts

When the oxygen content of the gas feed is increased, the performance of the Au/Al_2O_3 catalysts is improved in terms of conversion. A higher O_2 content does not influence the adsorption of the NH_3 [14]. Hence, probably the surface is mainly covered with

NH_3 and the reaction is very dependent on the availability of oxygen atoms. This is probably also the reason for the beneficial effect of addition of ceria, which is known to be able to provide and store oxygen. When Li_2O is added an improvement of activity is measured for the gold catalysts whereas on the copper and silver catalysts hardly any difference was noted. A possible role of the Li_2O is decreasing the surface acidity of the γ-Al_2O_3. It is expected that on a less acidic surface the NH_3 adsorption is hindered, which can give room for more oxygen adsorption on the support. This is supported by the observation that a post treatment of NaOH increases the activity of several catalysts in this reaction [4, 5]. The mechanistic route to N_2, NO and N_2O is considered in literature to proceed via a sequential NH_3 dissociation (hydrogen abstraction) [7, 26]. Amblard et al. [7] stated a mechanism in which surface NO_x can be reduced by surface NH_x. They considered the activation of surface NH_x to be the rate limiting step. As the addition of CeO_x to the Au/Al_2O_3 catalyst affects besides the activity also the selectivity of the catalyst, it is possible that CeO_x also affects the activation of surface NH_x. In an earlier paper [14] it is shown with FTIR measurements that gold seems to enhance the H-abstraction of NH_3 and from the observation that the selectivity of the ammonia oxidation is dependent on the CeO_x additive, it can be concluded that all components of the catalysts have an influence on the selectivity, suggesting that the chemical reactions may take place at the metal-support interface.

3.4.4 Comparison of the copper, silver and gold catalysts

If the activity and selectivity of the silver and copper catalysts are compared to the results of the gold catalysts published earlier by our group [12, 14, 15], some similarities are observed. For all three catalysts the addition of CeO_x or CeO_x + Li_2O is beneficial for the activity. In all cases the multicomponent catalyst with both oxides is the most active one. Possibly, the metal oxides have an important role in the ammonia oxidation chemistry. The copper, silver and gold metals are needed to create active catalysts as the supports only are inactive at temperatures below 400°C as shown in the present study and in [14]. These results may suggest that for all three metals used the reaction takes place at the metal-support interface. In addition for all three metals (copper, silver and gold) the size of the particles is important. For gold the particle size is crucial for the high oxidation activity [27]. The catalysts with copper nanoparticles also show an improved activity compared to literature data in which large Cu particles (10nm) have been used [5, 23]. For the silver catalysts the selectivity is improved if smaller particles are used. In terms of selectivity, copper and silver

catalysts differ from the gold catalysts. Addition of ceria to the Au/Al_2O_3 influences the selectivity, whereas the selectivity of copper and silver containing catalysts was not affected by CeO_x. A study by Lin et al. [14] showed that the catalytic ammonia oxidation activity of gold catalysts does not strongly depend on the average gold particle size, but is strongly influenced by the nature of the additive, which suggests a certain metal-support interaction which not only influences the activity but also the selectivity. Possibly, both the gold and ceria play an active role in the NO and N_2O production. On the silver and copper based catalysts the additive ceria only influences the activity but not the selectivity.

3.5 Conclusions

Based on the results presented above, it is concluded that silver and copper catalysts are very active and selective in the selective oxidation of ammonia to nitrogen. For both metals the interaction or nature of the support greatly influences the activity. Addition of Li_2O results in smaller particles for silver and copper, as was reported before for gold based catalysts. Addition of CeO_x increases the activity of the silver, gold and copper catalysts and for the gold catalysts influences also the selectivity. The particle size of the copper, silver and gold is very important for high activity and selectivity.

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4

A comparative study of oxidation of methanol on γ-Al_2O_3 supported group IB metal catalysts

Results are presented concerning the behavior of alumina supported Cu, Ag and Au (M) catalysts and the effect of addition of Li_2O and CeO_x on the oxidation of methanol. The γ-Al_2O_3 used is able to dehydrogenate methanol to formaldehyde and the addition of a metal to the support increases the CO production. A two-step reaction mechanism is proposed: in the first step, CH_3OH is dehydrogenated on alumina to formaldehyde. In the second step, the formaldehyde reacts on M to CO or CO_2. Another mechanism is proposed for good oxidizing catalysts: methanol reacts directly on M and is oxidized to CO_2. The addition of the co-catalyst CeO_x to the catalysts has a beneficial effect on the oxidation of methanol to CO_2 because of its ability to provide oxygen. We suggest that Li_2O blocks the adsorption site for methanol on alumina, and hence, decreasing the formation of formaldehyde.

4.1 Introduction

Methanol is used as a precursor for various industrial bulk chemicals, such as formaldehyde and larger hydrocarbons. Its worldwide annual production exceeds 37 million ton [1].

Due to the large demand for formaldehyde for the production of resins and larger base chemicals, an efficent catalytic process to produce formaldehyde is needed. Nowadays, the commercial BASF-process based on silver is still used to produce formaldehyde, although Fe/Mo-based catalysts gain ground. Studies by Lefferts et al. [2] showed that the silver-oxygen interaction is very important in the methanol dehydrogenation and is very sensitive to the silver surface morphology.

Methanol can also be used as a storage medium for hydrogen in cars, because of its relatively high hydrogen content and its fluidity. In principle hydrogen can be stored in various other ways, such as in the form of metal hydrides or as compressed liquefied H_2, the existing fueling infrastructure favors the use of methanol and it also introduces less potential safety hazards. Methanol can be oxidized on site to form CO, CO_2 and H_2 of which the latter can be used in a fuel cell. The formation of CO has to be avoided, because it poisons the catalytic Pt-sites in the PEM fuel cell. So, an extra catalyst that selectively oxidizes CO in the presence of hydrogen is necessary. However a catalyst that is selective to only CO_2 and H_2 is a better alternative.

In this report the dehydrogenation and oxidation of CH_3OH by IB-metals supported on γ-Al_2O_3 has been investigated. An earlier study in literature concerning the oxidation of methanol over Au, Ag and Cu on Fe_2O_3 [3,4] showed that all these three metals are active in oxidation of methanol and that the choice of the support is very important for the catalytic performance. Sciré et al. [4] stated that the high activity of the investigated catalysts is related to the enhancement of the reducibility of the support by weakening the metal-oxygen bond of the support and, thus, increasing the mobility/reactivity of the surface lattice oxygen.

In addition, the promoting effect of adding Li_2O and CeO_x has been investigated. A study by Ross et al. [5, 6] showed that addition of Li_2O or CeO_x greatly influences the reaction of methanol on copper based catalysts. A detailed study of Gluhoi et al. [7, 8] on the effects of addition of (earth) alkali metals to an Au/Al_2O_3 catalyst revealed that the main role of the (earth) alkali metals is to stabilize the gold nanoparticles i.e. that of a structural promoter in the investigated reactions. Comparable results have been found for copper and silver based catalysts [9]. Highly dispersed gold on suitable metal oxides exhibits extraordinarily high activity in vari-

ous low-temperature oxidation reactions [10–13]. Previously reported results show that ceria has a promoting effect on the activity of the Au/Al_2O_3 catalyst in the CO oxidation [13, 14]. It was argued that the active oxygen was supplied by the ceria, rather than from the gas phase. Moreover it was reported that the size of the ceria particles has a great influence on the activity of the catalyst [15].

In literature, methanol oxidation has been studied on various catalysts. The results have been reviewed by Tatibouët [16]. Depending on the catalyst nature and reaction conditions methanol oxidation may result in various products. This property of the methanol oxidation reaction has been used in the reverse process of probing the catalytic surface with this reaction and deducing the nature of the active oxygen. The reaction was found to be structure sensitive and appears to be a good test reaction to study the acidic and oxidation properties of oxide catalysts [16–19]. In contrast to many published studies concerning the total oxidation of methanol [3, 4, 20], in the present comparative study a methanol/O_2 ratio of 1 was used. This ratio permits to compare the behavior of Cu, Ag and Au nanoparticles on γ-Al_2O_3 in both partial oxidation and total oxidation. In addition, we have studied the dehydrogenation of methanol in the absence of O_2 in the feed.

4.2 Experimental

4.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x), Li_2O with alumina were prepared by pore volume impregnation of γ-Al_2O_3 (BASF, de Meern) with the corresponding nitrates. After calcination at 350°C these oxides were used as supports for the catalysts. The prepared mixed oxides have an intended Ce/Al and Li/Al ratio of 1/15. The copper and gold catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent [21]. An appropriate amount of $HAuCl_4$.3aq (99.999% Aldrich chemicals),$AgNO_3$ or $CuNO_3$.3aq was added to a suspension of purified water containing γ-Al_2O_3 or the mixed oxide. The intended M/Al ratio atomic was 1/75 (M=Cu,Ag or Au). This ratio of 1:75 is equal to 0.53at% M and resulted in 5wt% for gold, 2.5wt% for silver and 1.5wt% for copper. The temperature was kept at 80 °C allowing urea (p.a.,Acros) to decompose ensuring a slow increase of pH. When a pH of around 8-8.5 was reached the slurry was filtrated and washed thoroughly with water and dried overnight at 80 °C. Because urea and silver atoms can form a soluble $Ag[NH_3]^+$ complex a large surplus of silver was needed to deposit enough silver on

the Al_2O_3. The catalysts were thoroughly ground to ensure that the macroscopic particle size was around 200μm for all the catalysts used in this study. Prior to the activity measurement all catalysts were reduced at 400°C with hydrogen for 2 hours.

4.2.2 Catalyst characterization

The metal loading was verified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Varian Vista-MPX. For that purpose a small fraction of the catalyst was dissolved in diluted aqua regia. X-ray diffraction measurements were done using a Philips Goniometer PW 1050/25 diffractometer equipped with a PW Cu 2103/00 X-ray tube operating at 50kV an 40mA. The average particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [22].

4.2.3 Activity measurements

The activity and selectivity was determined using a flow reactor system equip-ped with a HP 5890 series II gas chromatograph. This system contained a set of flow controllers (*Brooks*) to ensure a steady gas flow, a mixing chamber to mix the gases, a vessel containing liquid methanol through which gases were bubbled and a quartz micro-reactor with oven. 200 mg catalyst was used for activity measurements. The catalyst was pre-treated in a hydrogen-flow and heated up to 300 °C for 2.5 h. After pre-treatment, the catalyst was exposed to a 23.75 mL min^{-1} flow of 4 vol-% oxygen in He and methanol. The oxygen-helium gas mixture was bubbled through a vessel containing methanol at room temperature, which resulted in an methanol/O_2 ratio of 1:1. The product gas mixture was analyzed using a HP 5890 series II gas chromatograph equipped with a molsieve 13x column (*Alltech*) for O_2, CO, CO_2 and H_2O separation and a Hayesep Q (*Alltech*) for CH_2O and CH_3OH separation. Detection of H_2-gas was not possible with this system. A TCD-detector was used for analysis. The measurements consisted of at least two heating/cooling cycles from room temperature to 400 °C at a rate of 2 °C min^{-1}.

Table 4.1: Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Metal loading (at%)	Average particle size (nm)
Au/Al_2O_3	4.8±0.1	0.51	4.5±0.1
$Au/CeO_x/Al_2O_3$	4.0±0.2	0.42	3.3±0.3
$Au/Li_2O/Al_2O_3$	4.5±0.3	0.48	<3.0
$Au/CeO_x/Li_2O/Al_2O_3$	4.0±0.2	0.42	<3.0
Ag/Al_2O_3	2.2±0.1	0.47	4.9±0.2
$Ag/CeO_x/Al_2O_3$	1.8±0.1	0.39	3.9±0.2
$Ag/Li_2O/Al_2O_3$	2.2±0.1	0.47	<3.0
$Ag/CeO_x/Li_2O/Al_2O_3$	1.6±0.1	0.34	<3.0
Cu/Al_2O_3	1.3±0.1	0.46	3.6±0.3
$Cu/CeO_x/Al_2O_3$	1.0±0.1	0.35	<3.0
$Cu/Li_2O/Al_2O_3$	1.4±0.1	0.49	<3.0
$Cu/CeO_x/Li_2O/Al_2O_3$	1.0±0.1	0.35	<3.0

4.3 Results

4.3.1 Characterization

The average particle size of the fresh catalysts could not be determined by XRD because the size of the particles was below the detection limit of 3nm. The results of the characterization of the catalysts after the reaction are shown in table 4.1. The catalysts without additives contain small particles of 3-4nm. With CeO_x and Li_2O added the average particle size is lower than the detection limit (3nm). HRTEM data of comparable catalysts have been published in earlier papers of our group [8, 23, 24]. The actual metal loading was almost equal to the intended metal loading. In addition, we have checked the catalysts for the Li and Ce contents with ICP-OES. These measurements showed that the appropriate amount of Li and/or Ce was deposited on the catalysts. The used γ-Al_2O_3 support was investated with XRF to determine which impurities are present. Three impurities were found: Na_2O(0.05wt%), SiO_2(0.1wt%) and Fe_2O_3(0.05wt%).

4.3.2 Activity of support materials and effect of oxygen

In figs. 4.1 and 4.2 the conversion of methanol by the support oxides is shown. The selectivity is shown as well. The alumina used converts CH_3OH above 225 °C selectively to formaldehyde. Maximum conversion is found above 300 °C. Adding CeO_x increases the temperature at which CH_3OH starts to decompose to 250 °C. Addition of Li_2O decreases maximal conversion to 50 % at 400 °C. When both CeO_x and Li_2O are added, behavior intermediate of those of Li_2O/Al_2O_3 and ceria/Al_2O_3 is observed. CH_3OH-conversion starts at 300 °C. The selectivity to formaldehyde decreases to 5 % above 250 °C, while selectivity to CO increases to 55 % and a 40% selectivity toward CO_2 is obtained. Addition of Li_2O results in a decrease of the selectivity to formaldehyde to 10 %, and the selectivity to CO is increased to 80 %. When both CeO_x and Li_2O are added, selectivities resemble those of Li_2O/γ-Al_2O_3 with a higher selectivity to CH_2O (30 %). The activity of the used alumina support from BASF with impurities(Na_2O, SiO_2 and Fe_2O_3) is compared to a sample of pure Al_2O_3 (Aldrich) with similar surface area. The results are presented in figure 4.3. The γ-Al_2O_3 with impurities has a much higher activity compared tot the pure alumina. However there is no difference was found in selectivity. Both supports produce mainly formaldehyde. Some CO is formed above 350°C.

In figure 4.4 the performance of the different supports in the absence of oxygen are presented. On the industrial Al_2O_3 and CeO_x/Al_2O_3 supports the conversion starts at 200°C and reaches maximum conversion of 75% at 400°C. The Li_2O containing supports show only minor methanol conversion at temperature above 300°C with at maximum conversion of 40%. Compared to the measurements with oxygen in figures 4.1 and 4.2 the methanol conversion is dropped, but the selectivity is not significantly affected by oxygen. Formaldehyde is the sole product in the absence of O_2.

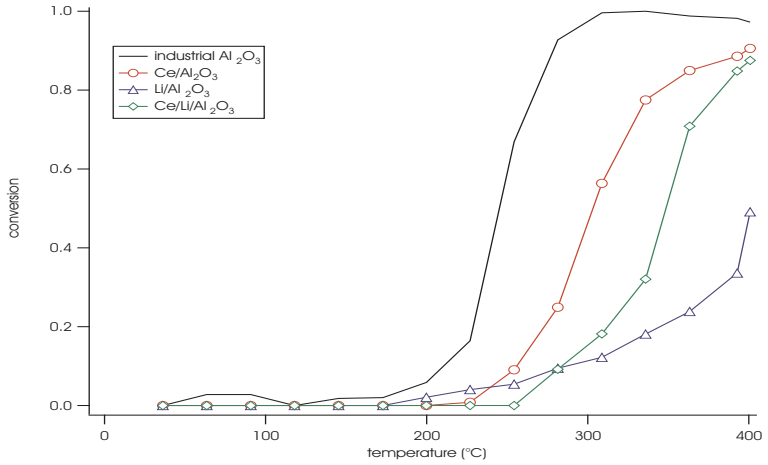

Figure 4.1: Conversion of methanol on different metal supports. CH_3OH:O_2 ratio of 1:1

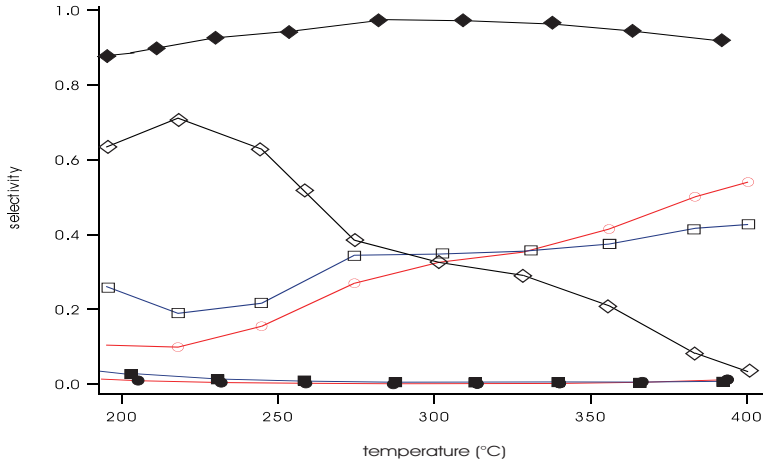

Figure 4.2: Product distribution vs temperature during methanol oxidation over Al_2O_3 (full symbols) and CeO_x/Al_2O_3 (open symbols): S_{CH_2O} (♦), S_{CO} (●), S_{CO_2} (■) CH_3OH:O_2 ratio of 1:1

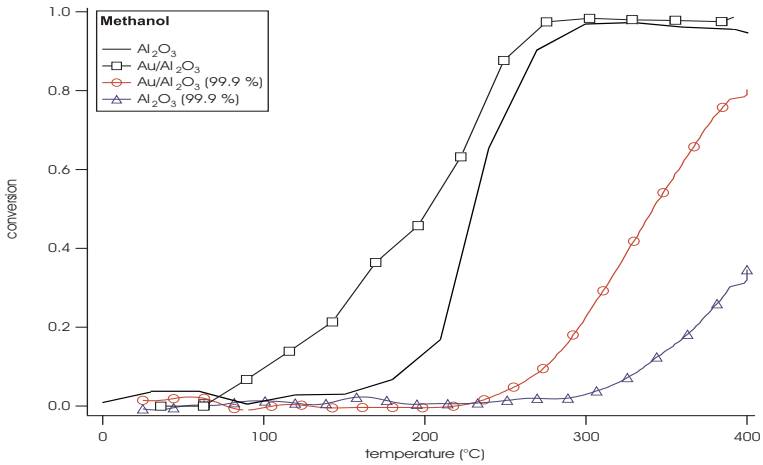

Figure 4.3: Conversion of methanol over γ-Al_2O_3 and Au/Al_2O_3 using on industrial- and reagent grade γ-Al_2O_3 support and on pure γ-Al_2O_3 (99.9%). CH_3OH:O_2 ratio of 1:1

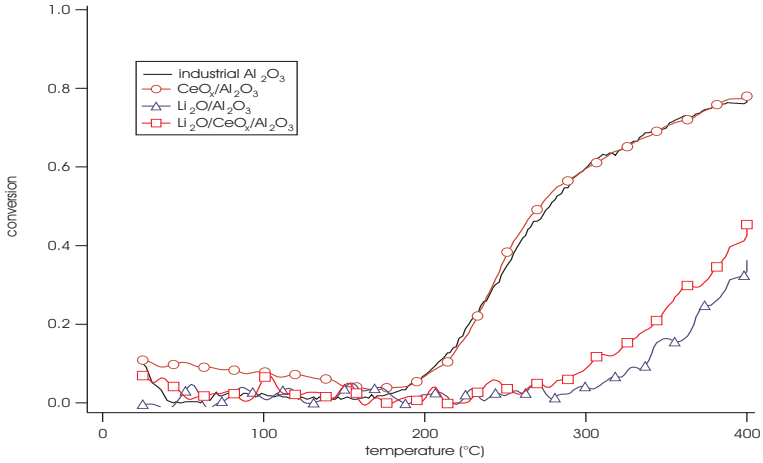

Figure 4.4: Conversion of methanol in the absence of oxygen on different supports

4.3.3 Effect of Cu, Ag and Au addition using different supports

In figures 4.5, 4.6 and 4.7 the performance of by Cu, Ag and Au on the γ-Al_2O_3 in the oxidation of methanol is shown. It can be seen from fig. 4.5 that Au/Al_2O_3 is the most active catalyst and that CH_3OH-oxidation starts at 100 °C. Maximum conversion reaches 100% at 275 °C. On copper the CH_3OH conversion starts at 150 °C and reaches 100 % conversion at 300 °C. The CH_3OH-conversion on silver starts at 200 °C and reaches maximum conversion at 350 °C.

Clearly, the effect of addition of Cu and Ag on the methanol conversion is small. However, the effect on the selectivity is huge. Gold is selective to both CH_2O (60 %) and CO_2 (40 %) at reasonable levels of methanol conversion. Selectivity to CO increases slowly to 40 % above 300 °C. Silver shows equal selectivity to formaldehyde and CO_2 (50 %) above 250 °C and shows a slight increase of selectivity to CO above 250 °C. On copper high selectivity to CO_2 (up to 100 %) is seen, while selectivity to formaldehyde and CO does not exceed 20 %. Between 200 and 300 °C an increase of selectivity to CH_2O (to 20 %) is seen, which is also observed with the copper-catalysts and with some gold-catalysts as well.

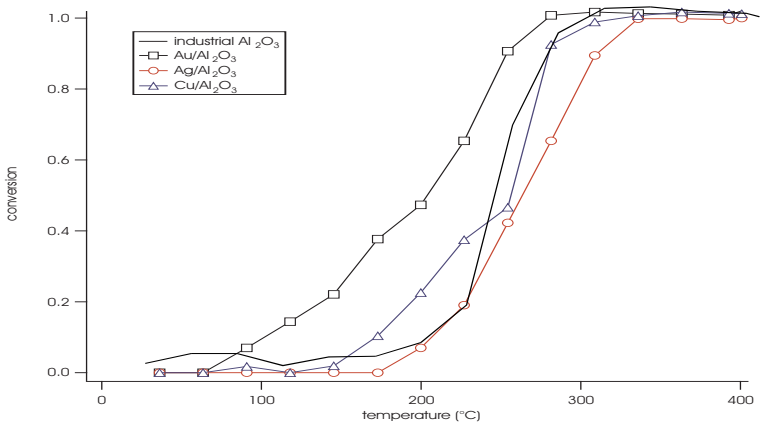

Figure 4.5: Conversion of methanol on different metal catalysts. CH_3OH:O_2 ratio of 1:1

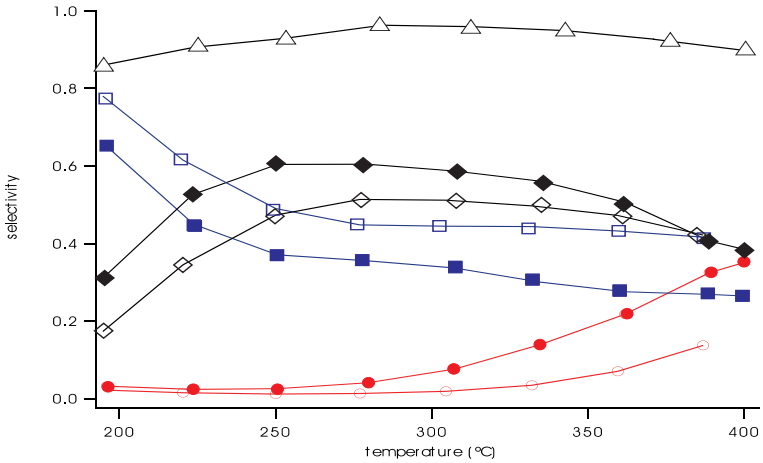

Figure 4.6: Product distribution vs temperature during methanol oxidation over Au/Al_2O_3 (full symbols): S_{CH_2O} (♦), S_{CO} (●), S_{CO_2} (■) Ag/Al_2O_3 (open symbols): S_{CH_2O} (◊), S_{CO} (○), S_{CO_2} (□) and γ-Al_2O_3: S_{CH_2O} (△). CH_3OH:O_2 ratio of 1:1

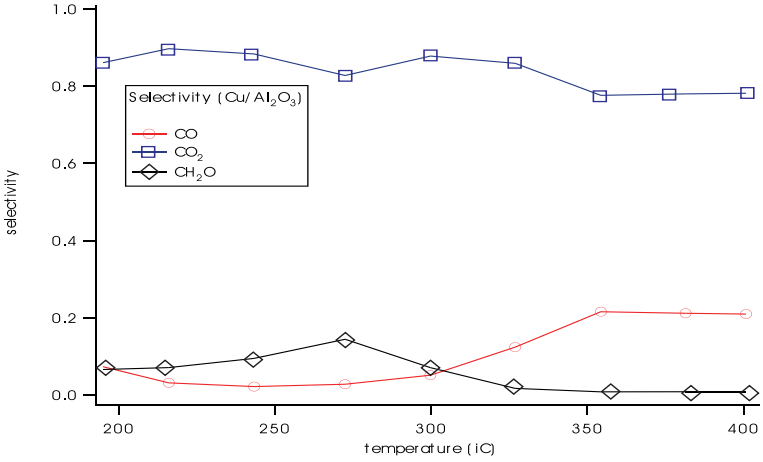

Figure 4.7: Product distribution vs temperature during methanol oxidation over Cu/Al_2O_3:S_{CH_2O} (♦), S_{CO} (●), S_{CO_2} (■)

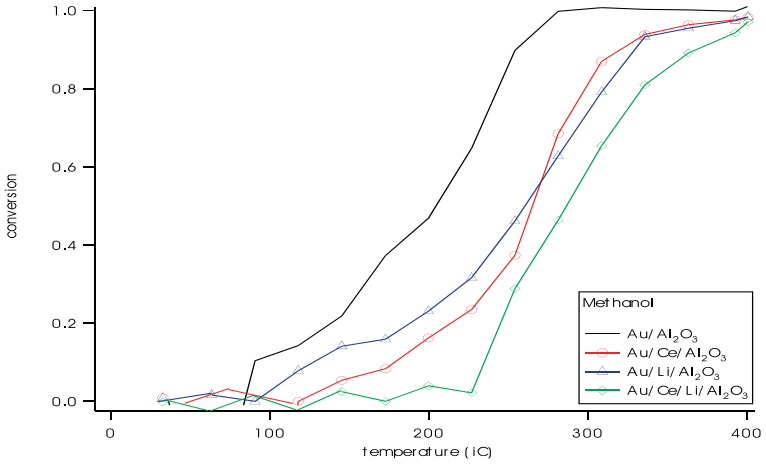

Figure 4.8: Conversion of methanol on Au based catalysts on different metal supports CH_3OH:O_2 ratio of 1:1

In figures 4.8 and 4.9, the effect of ceria and Li_2O on the performance of Au/Al_2O_3 is shown. It can be seen from fig. 4.8 that Au/Al_2O_3 is active above 100 °C and 100% conversion is obtained above 275 °C. When CeO_x and/or Li_2O are added an increase in temperature of 50°C is needed to obtain the same conversion. However, a large increase in activity is observed compared to the support materials. The supports only show activity above 250 °C, while after the addition of gold, the T50 % lies around 200 °C. The largest increase in performance due to the noble metal is seen for the lithium containing support.
From figure 4.6 it can be seen that Au/Al_2O_3 has a high selectivity (60 %) to formaldehyde at temperatures above 200 °C. By adding CeO_x and/or Li_2O this selectivity is decreased to under 20 % as shown in figure 4.9. Clearly in the presence of gold the selectivty shifts to total oxidation of methanol. The selectivity to CO is slightly decreased by adding CeO_x and/or Li_2O. Notice also the increase in selectivity to formaldehyde at temperature between 180 and 300 °C on $Au/Li_2O/\gamma$-Al_2O_3 and $Au/CeO_x/\gamma$-Al_2O_3. This behaviour is encountered with copper-catalysts as well. Compared to the support materials, the selectivity to CO_2 increased up to 85 %. The formation of CO above 350 °C is also increased due to Au.

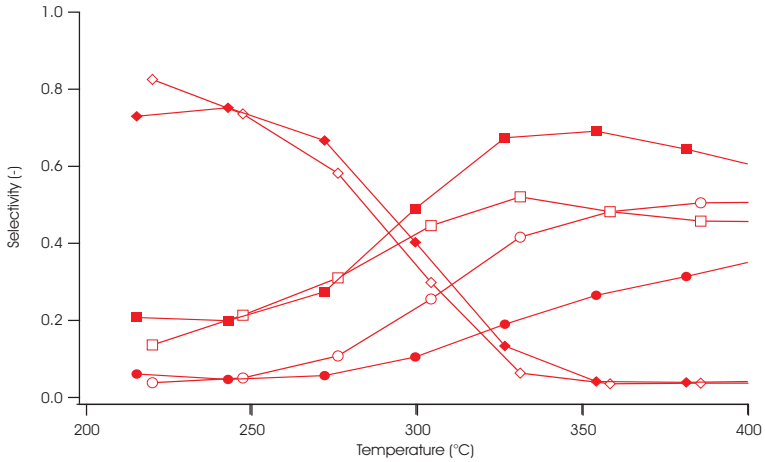

Figure 4.9: Product distribution vs temperature during methanol oxidation over $Au/Li_2O/Al_2O_3$ (full symbols) and $Au/CeO_x/Al_2O_3$ (open symbols): S_{CH_2O} (♦), S_{CO} (●), S_{CO_2} (■) CH_3OH:O_2 ratio of 1:1

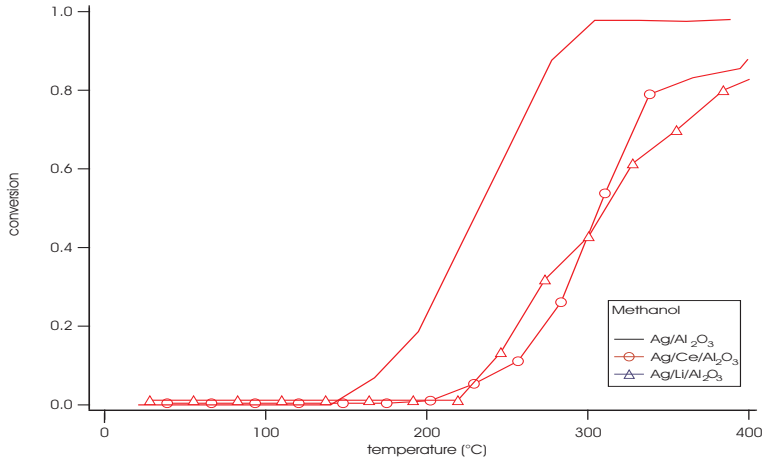

Figure 4.10: Conversion of methanol on Ag based catalysts on different metal supports CH_3OH:O_2 ratio of 1:1

In figures 4.10 and 4.11 the conversion of methanol over Ag-catalysts on different support oxides is shown. The selectivity to possible products is shown as well. It can be seen from figure 4.6 that Ag/γ-Al_2O_3 shows CH_3OH-conversion above 200 °C, and reaches maximum conversion (90 %) at 350 °C. After addition of CeO_x or Li_2O CH_3OH-conversion starts at significantly higher performance of 250 °C. These values are rather similar to the values for the support materials. However a large increase in maximum conversion of the lithium containing support is observed: due to the addition of Ag, the maximum conversion is increased to 100 %. From figures 4.6 and 4.11 it can be seen that Ag/γ-Al_2O_3 has an equal selectivity to formaldehyde and CO_2 (50 %). By adding CeO_x the selectivity to formaldehyde is lowered slightly to 40 %. It also increases the CO production. Adding Li_2O increases selectivity to CO_2 to 80 % up to 300 °C and increases the temperature where formaldehyde production (up to 40 %) begins. Compared to the support materials, the silver catalyst show less selectivity to CO.
In figures 4.12, 4.13 the oxidation of methanol over Cu-catalysts on different support oxides is shown. The selectivity of different catalysts to possible products is shown as well. Fig. 4.12 shows that CH_3OH-conversion on Cu/γ-Al_2O_3 starts at 150 °C, reaching its maximum at 300 °C. Adding CeO_x tends to rise the starting temperature of CH_3OH-conversion, but has no effect on maximum conversion. Addition of Li_2O decreases the maximum conversion to 50 % at 400 °C. The observed conversions are rather similar to those of the support materials, although the conversion of the Cu/ γ-Al_2O_3 catalyst starts at lower temperatures. From figs. 4.7 and 4.13 it can be seen that copper-catalysts show a high selectivity (85 %) to CO_2. Adding Li_2O decreases the CO-formation at high temperatures (up to 30 %). Notice the increase in selectivity to formaldehyde between 200 and 300 °C. This behaviour is encountered for all copper catalysts and some gold catalysts. Copper increases the selectivity to CO_2 to 95 % compared to the support materials.

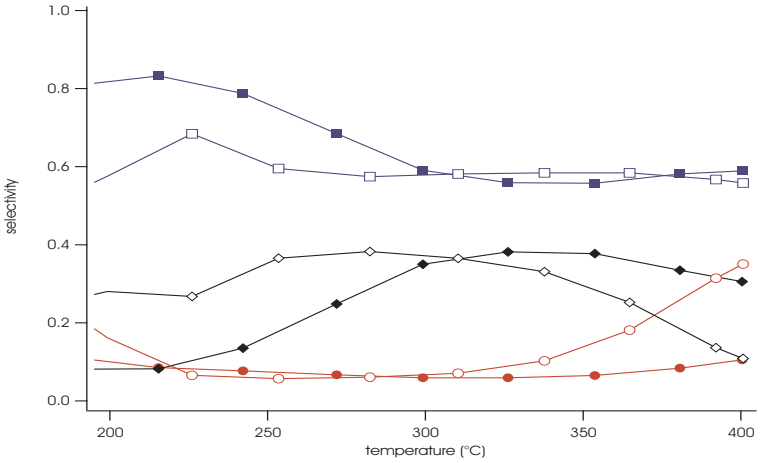

Figure 4.11: Product distribution vs temperature during methanol oxidation over $Ag/Li_2O/Al_2O_3$ (full symbols) and $Ag/CeO_x/Al_2O_3$ (open symbols): S_{CH_2O} (♦), S_{CO} (●), S_{CO_2} (■) CH_3OH:O_2 ratio of 1:1

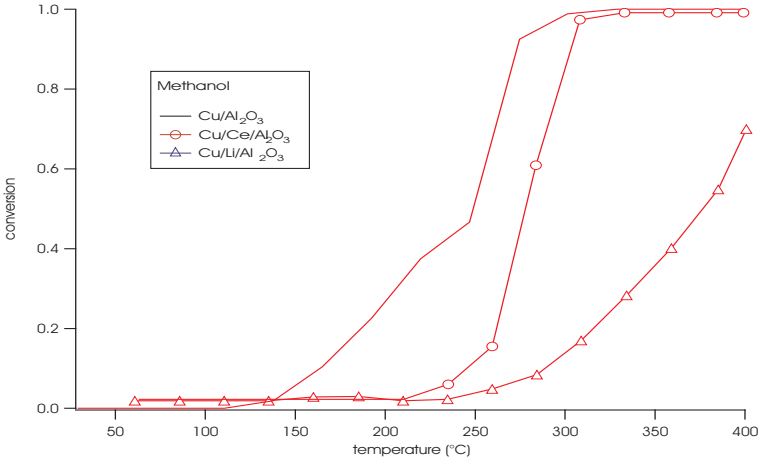

Figure 4.12: Conversion of methanol on Cu based catalysts on different metal supports CH_3OH:O_2 ratio of 1:1

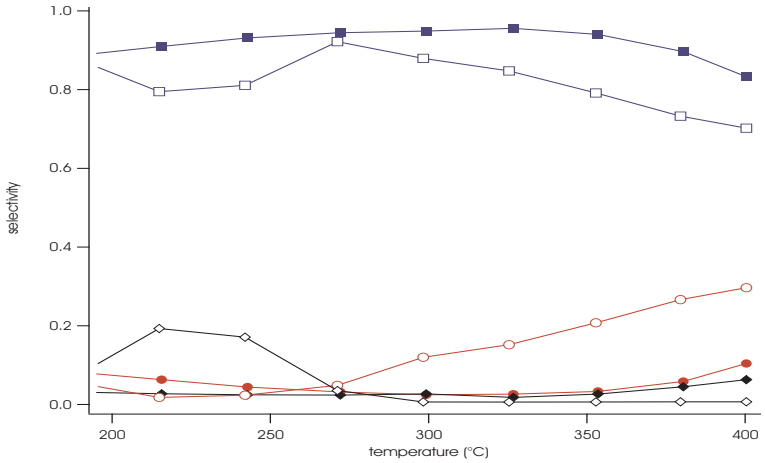

Figure 4.13: Product distribution vs temperature during methanol oxidation over $Cu/Li_2O/Al_2O_3$ (full symbols) and $Cu/CeO_x/Al_2O_3$ (open symbols): S_{CH_2O} (⧫), S_{CO} (●), S_{CO_2} (■) $CH_3OH:O_2$ ratio of 1:1

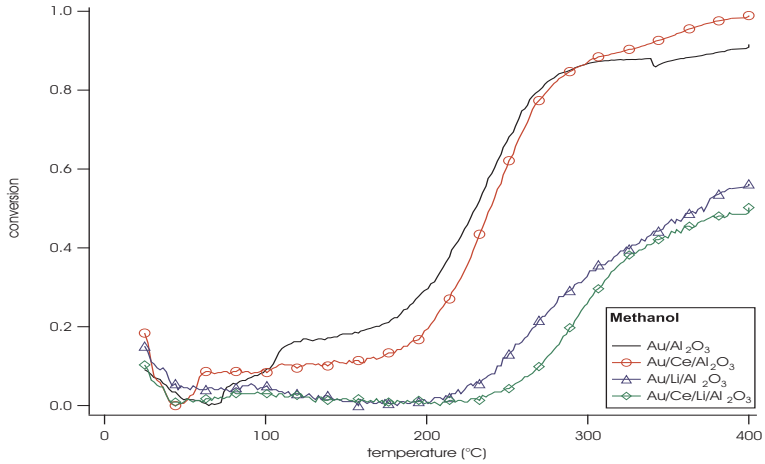

Figure 4.14: Conversion of methanol in the absence of oxygen on Au-catalysts on different supports $CH_3OH:O_2$ ratio of 1:1

4.3.4 The effect of oxygen on supported gold catalysts

In figures 4.14, 4.15 and 4.16 are shown the results of the measurements of the methanol only flow over the gold based catalysts. Upon comparison to figure 4.4 which depict the results of the different supports, it is clear that the addition of gold has a significant contribution to the activity of the catalysts. A striking effect is found for Li_2O, a maximum conversion of 50% is found in the presence of Li_2O, whereas in the absence of Li_2O a conversion of almost 100% is found. As can be seen from figs. 4.15 and 4.16. Au/γ-Al_2O_3 and Au/CeO_x/γ-Al_2O_3 have a high selectivity (90 %) to formaldehyde at temperatures below 300 °C. Above this temperature the selectivity decreases to 40 % on gold with an increase in the selectivity towards CO. Addition of CeO_x results in formation of CO_2 with a selectivity up to 60 % above 300 °C. All catalysts show an increased selectivity (up to 60 %) to CO at temperatures above 300 °C. Adding both CeO_x and Li_2O decreases the selectivity to formaldehyde to 60 %, with an increase of selectivity to CO_2. For the Au/γ-Al_2O_3 support also a long during experiment was done for 65h at 300 °C with methanol in the absence of oxygen. This resulted in a stable 88% conversion and a selectivity to CH_2O of 90%, without apparent coke forming.

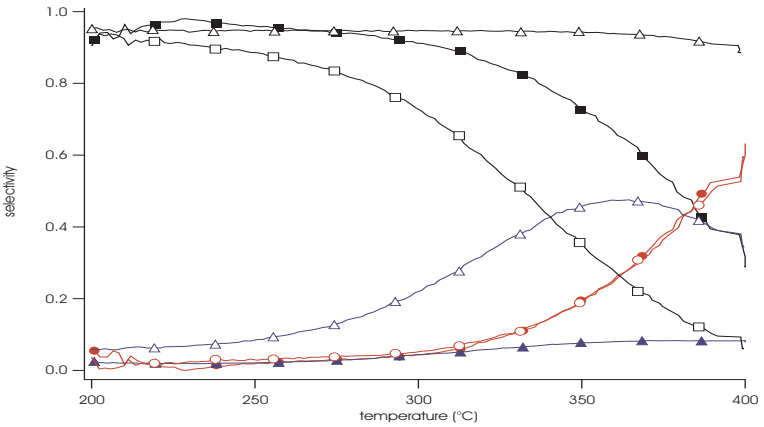

Figure 4.15: Product distribution vs temperature during methanol dehydrogenation over Au/Al_2O_3 (full symbols) and Au/CeO_x/Al_2O_3 (open symbols): S_{CH_2O} (■), S_{CO} (●), S_{CO_2} (▲)and the S_{CH_2O} over Al_2O_3:△ CH_3OH:O_2 ratio of 1:1

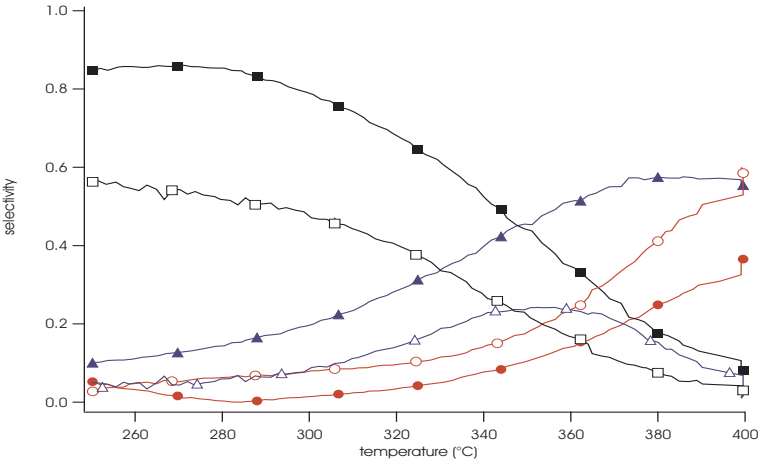

Figure 4.16: Product distribution vs temperature during methanol dehydrogenation over Au//CeO_x/Al_2O_3 (full symbols) and Au/$Li_2O/CeO_x/Al_2O_3$ (open symbols): S_{CH_2O} (■), S_{CO} (●), S_{CO_2} (▲) CH_3OH:O_2 ratio of 1:1

4.4 Discussion

4.4.1 Activity of the bare supports and effect of oxygen

The most active support in this study is the acidic γ-Al_2O_3 that is able to produce formaldehyde, with high selectivity. The presence or absence of O_2 does not seem to have a big influence on this selectivity. A part of the activity of the commercially γ-Al_2O_3 support used, might be attributed to the presence of impurities, as very pure γ-Al_2O_3 exhibits a much lower activity in the reaction with methanol. It is not clear whether the activity is caused by the intrinsic catalytic activity of the impurities or by the influence of the impurities on the γ-Al_2O_3. Cariati et al. [20] found CO to be the principal product on Al_2O_3. They used a flow of 20% O_2 and 5.5% CH_3OH, which is a much higher oxygen content than we used. So the high selectivity to formaldehyde found in our studies is probably related to the small or absent oxygen content in the reaction flow. The rate determining step of formaldehyde formation was found to be the C-H bond breaking of the adsorbed methoxy species [16]. The ability to break

a C-H bond will depend on the basic or nucleophilic character of oxygen species in proximity of the methoxy group [16]. The desorption of reaction products will be favored by weak acid sites [25]. For CH_2O formation both weak acid and weak basic sites are needed to limit the H abstraction and prevent strong adsorption. This is clearly the case for the Al_2O_3 support. When Li_2O, which has a basic character, is added the methanol conversion is greatly decreased and the selectivity to CH_2O goes to zero. Instead CO and CO_2 are formed. This indicates further oxidation of formaldehyde to HCOOH due to the increased basic character [16]. This HCOOH is dehydrated to CO or further oxidized to CO_2 with oxygen. Addition of CeO_x to Al_2O_3 results in a small decrease in methanol conversion. This catalyst shows selectivity to CO and CO_2 at the expense of CH_2O, which is further oxidized. This can be attributed to the oxygen atoms of the ceria available for the oxidation reaction. Although oxygen is not needed for the CH_2O formation it seems to increase the methanol conversion and so increases the formaldehyde production. Possibly, small amounts of oxygen can prevent deactivation of the catalytic surface.

4.4.2 Gold catalysts

Addition of gold to all used supports results in an enhanced methanol conversion. The effect is most pronounced for the Li_2O/Al_2O_3 support where the onset temperature is lowered from 250°C to 150°C. The smallest effect is for the ceria containing catalysts, where also the selectivity is hardly affected by the gold. In contrast Scirè et al. found a great improvement by adding gold to ceria in total oxidation of methanol [4]. They claimed that gold weakens the Ce-O bond and thus increases the mobility/activity of the surface lattice oxygen. In our measurements no evidence is found for such an effect. However, it should be emphasized that we did not use pure CeO_x as support but CeO_x/Al_2O_3. It might be that in our system the Ce-O bond is already weakened by the γ-Al_2O_3 support or that the ceria is more reduced into Ce^{3+} in our oxygen lean conditions. Scirè et al. used an excess of oxygen with a methanol to oxygen ratio of 0.7:10. In our opinion methanol is converted to formaldehyde on the support and further oxidized on the metallic gold particles to CO and CO_2. The selectivity to formaldehyde of the gold catalyst is comparable to that of the γ-Al_2O_3-support (fig. 4.2). Addition of gold affects the T50 % temperature - and therefore the activity - positively. It can be seen that adding gold does not change the selectivity of oxidation of methanol to formaldehyde by alumina below 350 °C. Adding gold does increase the selectivity to CO above this temperature. Only above this temperature CO is

formed. This effect is caused by gold particles, because this increase is not observed using pure alumina. These observations suggest a possible mechanism of CH_3OH oxidation: methanol is first decomposed to formaldehyde on the alumina support at low temperatures. When the temperature increases formaldehyde is oxidized on gold to CO. This suggests that gold is not active in formaldehyde formation below 350 °C. While no increase of CO_2 production is observed above 350 °C, gold does not oxidise CO further to CO_2, possibly this is caused by the lack of oxygen. An increase of selectivity to CO_2 in the whole temperature region is observed when gold is added. Probably another mechanism than the one described above takes place at the same time. CH_3OH is adsorbed directly on the gold, and oxidised fully to CO_2. This suggestion is supported by literature data [26], where O-H bond breaking was observed for methanol on the Au(310) surface.

When CeO_x is added to the catalyst, the selectivity to formaldehyde drops completely, while the selectivity to CO and CO_2 is increased to over 80 % (figs. 4.8, 4.9). Above 300 °C the formaldehyde is further oxidised to CO and CO_2 probably by the gold particles, assisted by the ceria, which can provide the oxygen necessary for complete oxidation and can act as a co-catalyst [23]. The results of the non-oxidative dehydrogenation of methanol show the same trend as the results with O_2. The Au/Al_2O_3 catalyst produces mainly CH_2O at temperatures up to 350 °C. Above this temperature the formaldehyde, which is probably formed on the support is further oxidized to CO by the gold particles. Measurements in the presence of oxygen showed a higher selectivity toward CO and CO_2. With the addition of metal oxides more CO and CO_2 are formed. This indicates further oxidation of the formed formaldehyde by the same reasons as mentioned above. The results on the Au/Al_2O_3 catalysts with O_2 produce more CO_2, so it is likely that oxygen is needed for the crucial step for the oxidation of formaldehyde to CO_2 on the metal particles.

4.4.3 Silver catalysts

The Ag/Al_2O_3 catalyst is more selective to CO_2 than γ-Al_2O_3, and it is equally active. While almost no increase in the production of CO is seen, it is suggested that silver is able to either oxidize formaldehyde that is formed on the alumina directly to CO_2 or oxidize methanol fully to CO_2. In order to do this, the oxidizing capabilities of the Ag-catalyst have to be better than that of Au-catalyst, which is normally not the case. Above 350 °C slightly more CO is formed compared to the alumina support, due to the addition of Ag. This increase is smaller than the increase that is seen with the

Au/Al_2O_3 catalyst. At these temperatures the selectivity to formaldehyde drops, while the selectivity to CO_2 remains the same. This suggests that formaldehyde is oxidized to CO, instead of CO_2. It also shows that two mechanisms take place at the same time: In the first mechanism CH_3OH is activated on the Ag-particles and oxidized directly to CO_2 at temperatures above 200 °C. In the second mechanism CH_3OH is activated on the alumina and converted to formaldehyde. The produced formaldehyde is then converted to CO on the silver, at temperatures above 350 °C.

The addition of silver to the Li_2O/Al_2O_3 support causes the formation of CH_2O at temperatures above 300°C. As the support only does not convert methanol into formaldehyde, the formation can be attributed to the silver particles. Addition of CeO_x to the Ag-catalysts leads to an increased selectivity to CO_2 (fig. 4.11), but still 40 % selectivity to formaldehyde is observed. Because CeO_x is known for its oxygen storage capacity, it is suggested that the oxygen supplied by ceria is used for full oxidation of methanol to CO_2. The high selectivity to formaldehyde might be explained by the worse oxidising capabilities of silver compared to gold. Above 350 °C the selectivity to CO increases, while the selectivity to formaldehyde drops. Formaldehyde formed on the alumina will be oxidized to CO on silver. This reaction is enhanced in comparison to the silver-only catalyst by the addition of ceria.

4.4.4 Copper catalysts

While addition of gold and silver do not alter the selectivity to formaldehyde very much compared to γ-Al_2O_3, addition of copper leads to 85 % selectivity to CO_2 (figure 4.7). Almost no formaldehyde is formed. This illustrates that Cu is more active in complete oxidation of CH_3OH than the other metals. At high temperatures not sufficient O_2 in the feed is available for complete oxidation to CO_2 and CO is formed. Addition of CeO_x does not affect the activity and the selectivity of the catalyst (fig. 4.13), because Cu/Al_2O_3 is already very efficient in total oxidation of methanol. When Li_2O is added to the Cu/Al_2O_3 catalyst, the conversion drops to 65 % at 400°C, while the selectivity to CO_2 remains 85 % (figure 4.13). Almost no CO is formed at high temperatures. As pure alumina shows a much higher conversion of methanol, it is suggested that the addition of Li_2O deactivates the catalytic activity of the support. This implies that the suggested mechanism plays a mayer role: if no formaldehyde can be formed on the support, it cannot be oxidised to CO_2 on copper.

4.4.5 Comparison of the copper, silver and gold catalysts

On all the three γ-Al_2O_3 supported Cu, Ag and Au catalysts the same mechanism can explain the results. Methanol is dehydrogenated on the support to formaldehyde and is further oxidized on the metal particles. Copper is most active in total oxidation and shows the highest selectivity to CO_2. The gold and silver based catalyst show similar behavior when γ-Al_2O_3 is used as support. The addition of Li_2O to Al_2O_3 results in a drastic decrease in formaldehyde formation. On the silver containing catalyst there is some selectivity to CH_2O at temperature above 300 °C, which is not observed for the gold containing catalyst, demonstrating that gold is better in total oxidation of methanol.

4.5 Conclusions

In the dehydrogenation and oxidation of methanol the support and additives play a major role in the activity and selectivity. It is suggested that the first step in the oxidation is the dehydrogenation of methanol into CH_2O on the acidic support: γ-Al_2O_3. Addition of Li_2O to the support diminishes this reaction. When Cu, Ag and Au particles are added oxidation of the formed formaldehyde is observed, leading to complete oxidation on Cu/Al_2O_3. The results of the $Ag/Li_2O/Al_2O_3$ catalyst suggest that silver particles are capable to oxidize methanol partially into formaldehyde. Addition of CeO_x results in an increased selectivity to CO and CO_2 and acts as a co-catalyst next to the deposited metal particles. In the absence of oxygen the presence of gold particles enhances the catalytic activity.

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5

Direct conversion of ethanol into ethylene oxide on copper and silver nanoparticles

Effect of addition of CeO_x and Li_2O

The behavior of nanoparticles of copper and silver on an alumina support in the oxidation and dehydrogenation of ethanol is investigated. Pure alumina mainly acts as an acidic catalyst and produces diethyl ether and ethylene. Addition of copper and silver nanoparticles results in a direct conversion of ethanol into ethylene oxide. Addition of Li_2O influences the selectivity by suppressing the formation of diethyl ether and ethylene. Using $Ag/Li_2O/Al_2O_3$ and $Cu/Li_2O/Al_2O_3$ catalysts it is possible to obtain high selectivity towards ethylene oxide at a temperature of 200°C. It is suggested that at low concentrations the main role of oxygen is to prevent coke formation on the catalytic surface. Addition of CeO_x results in higher selectivities towards CO.

5.1 Introduction

Selective oxidation of ethanol is increasingly receiving more attention as ethanol can be used for the synthesis of chemical intermediates in the manufacture of high-tonnage commodities. Ethanol can be converted to e.g. acetaldehyde, ethane, carbon monoxide/hydrogen and ethylene. The ethylene can be further converted over a silver based catalyst to ethylene oxide, which is one of the most important chemical intermediates. It is an intermediate for the production of ethylene glycol and for the production of polyester fibers and plastics such as polyethylene terephthalate (PET). This paper will show that ethanol can be converted directly into ethylene oxide at mild temperatures and atmospheric pressure, in addition to it total oxidation products carbon dioxide and water.

Ethanol is a simple probe molecule to study reactions on metal [1–3] and oxide surfaces [4, 5]. On most surfaces the ethanol molecules first dissociate to ethoxy species. These ethoxy species are further oxidized to acetaldehyde or dehydrated to ethylene. On metal surfaces acetaldehyde either desorbs or decomposes to CO and methane [6]. In some cases, coupling and bimolecular hydrogenation reactions occur resulting in production of higher hydrocarbons such as diethyl ether [7, 8].

In this study we investigated the low temperature activity of Cu/Al_2O_3 and Ag/Al_2O_3 catalysts in the dehydrogenation, dehydration and oxidation reaction of ethanol. In addition, the promoting effect of adding Li_2O and CeO_x has been investigated. CeO_x is an active oxide for the oxidation of CO to CO_2 and for making H_2 from ethanol by partial oxidation or steam reforming [9, 10]. In earlier papers we reported that (earth) alkali metals stabilize gold nanoparticles and hence, act as a structural promoter for Au/Al_2O_3 [11,12]. More recently, we reported that Cu and Ag nanoparticles on γ-Al_2O_3 can be stabilized in the same way [13, 14]. In another study of our group it was found that highly dispersed gold on suitable metal oxides exhibits interesting behavior toward the oxidation of ethanol and is capable of converting ethanol directly into ethylene oxide [15]. This motivated us to investigate the oxidation of ethanol over γ-Al_2O_3 supported copper and silver based catalysts. It is known for quite a long time that CuO-CeO_2 catalysts are very active and selective in CO (selective) oxidation [10, 16]. Ceria has a promoting effect on the activity of the Cu/Al_2O_3 and Ag/Al_2O_3 catalysts in methanol oxidation [14]. It was argued that the active oxygen was supplied by the ceria. The size of the ceria particles has a great influence on the activity of the catalyst [17].

The oxidative dehydrogenation of ethanol to acetaldehyde is known to be cata-

lyzed by materials possessing strong base sites such as Li_2O [18]. Earlier work of our group revealed that addition of Li_2O has great effect on the acidic sites of γ-Al_2O_3 and so influences the selectivity towards products which are not formed on these acidic sites [14,19]. In this paper we show that Li_2O promoted Ag en Cu particles supported on γ-Al_2O_3 can be used for the production of ethylene oxide from ethanol.

5.2 Experimental

5.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x) and/or Li_2O with alumina were prepared by pore volume impregnation of γ-Al_2O_3 (BASF) with the corresponding nitrates. After calcination at 350°C these oxides were used as supports for the Cu or Ag based catalysts. The prepared mixed oxides have an intended atomic ratio Ce/Al and Li/Al of 1/15. The copper and silver catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent. An appropriate amount of $Cu(NO_3)_2$.3aq or $AgNO_3$ was added to a suspension of purified water containing γ-Al_2O_3 or the mixed oxide. The intended M/Al atomic ratio was 1/75 (M=Cu or Ag). This ratio of 1:75 is equal to 0.53at% M and resulted in 2.5wt% for silver and 1.5wt% for copper. The temperature was kept at 80 °C allowing urea (p.a.,Acros) to decompose, ensuring a slow increase of pH. When a pH of around 8-8.5 was reached the slurry was filtrated and washed thoroughly with water and dried overnight at 80 °C. Because urea and silver atoms can form a soluble $Ag[NH_3]_2{}^+$ complex, a large surplus of silver was needed to deposit enough silver on the Al_2O_3. The catalysts were thoroughly ground to ensure that the macroscopic particle size was around 200μm for all the catalysts used in this study. Prior to the activity measurement all catalysts were reduced at 400°C with hydrogen for 2 hours.

5.2.2 Catalyst characterization

The metal loading was verified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Varian Vista-MPX. For that purpose a small fraction of the catalyst was dissolved in diluted aqua regia. X-ray diffraction measurements were done using a Philips Goniometer PW 1050/25 diffractometer equipped with a PW Cu 2103/00 X-ray tube operating at 50kV and 40mA. The average particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding

support by using the Scherrer equation [20].

5.2.3 Activity measurements

The amount of catalyst used was 200mg for the Ag/γ-Al_2O_3 and Cu/γ-Al_2O_3 catalysts. For the catalysts containing CeO_x and/or Li_2O the amount of catalyst was adjusted in such a way that the amount of metal atoms (Ag or Cu) was similar for all the catalysts with and without additives. Prior to activity experiments the catalysts were reduced with H_2 (4 vol% in Ar) at 400 °C for 2 hours. Activity tests of the catalysts were performed in a micro reactor system. An oxygen flow balanced in argon was bubbled through a vessel containing absolute ethanol. For the oxidation an ethanol oxygen ratio of 1:1 was used. For the decomposition reaction a argon flow was bubbled through the vessel. Typically, a total gas flow of 40ml^{-1}(GHSV $\approx$ 2500h^{-1})was maintained. The effluent stream was analyzed on-line by a gas chromatograph (HP 8590) with a CTR1 column (Alltech) containing a porous polymer mixture and an activated molecular sieve and a Hayesep Q column (Alltech). The experiments were carried out under atmospheric pressure. Each measurement is composed of multiple temperature programmed cycles of heating and cooling, with a rate of 2°C/min. Mass spectrometry confirmed that the analysis of the reaction products with GC was correct. Unless otherwise stated the results of the first cooling stage are depicted in the figures.

5.3 Results

5.3.1 Characterization

For the fresh Ag and Cu particles the average size could not be determined by XRD because the size of the particles was below the detection limit of 3nm. The results of the characterization of the catalysts after the reaction are shown in table 5.1. The catalysts without additives contain small particles of 3-4nm. With CeO_x and Li_2O added the average particle size is lower than the detection limit (3nm). HRTEM data of comparable catalysts have been published in earlier papers of our group [12, 21, 22]. The actual metal loading was almost equal to the intended metal loading. In addition, we have checked the catalysts for the Li and Ce contents with ICP-OES. These measurements showed that the appropriate amount of Li and/or Ce was deposited on the catalysts. The used γ-Al_2O_3 support was investigated with XRF to determine which

impurities are present. Three impurities were found: Na_2O(0.05wt%), SiO_2(0.1wt%) and Fe_2O_3(0.05wt%).

Table 5.1: Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Average particle size (nm)
Ag/Al_2O_3	2.3±0.1	4.5±0.1
$Ag/CeO_x/Al_2O_3$	1.7±0.1	3.3±0.1
$Ag/Li_2O/Al_2O_3$	2.2±0.1	<3.0
$Ag/CeO_x/Li_2O/Al_2O_3$	1.6±0.1	<3.0
Cu/Al_2O_3	1.5±0.1	3.5±0.1
$Cu/CeO_x/Al_2O_3$	1.0±0.1	<3.0
$Cu/Li_2O/Al_2O_3$	1.4±0.1	<3.0
$Cu/CeO_x/Li_2O/Al_2O_3$	1.0±0.1	<3.0

5.3.2 Activity of catalyst supports without metal particles

In table 5.2 the results are presented concerning the dehydrogenation of ethanol in the absence of oxygen, for the supports without Cu and Ag. The most active support is the γ-Al_2O_3 without additive. The main products are the dehydration products diethyl ether and ethylene. In addition, some trace amounts of acetaldehyde are found at temperatures up to 300°C. Addition of ceria to the γ-Al_2O_3 results in formation of CO at the expense of diethyl-ether and ethylene, at temperatures above 300°C. The formed hydrogen is converted to water. Addition of Li_2O to the alumina catalysts lowers the ethanol conversion compared to the γ-Al_2O_3-only catalyst, and results in a lower selectivity towards ethylene. No acetaldehyde is found. The catalysts which contain both Li_2O and CeO_x show a behavior typical of a mixture of Li_2O/Al_2O_3 and CeO_x/Al_2O_3 catalysts.

Similar measurements have been performed for an ethanol/O_2 mixture of 1 using the supports without Cu or Ag deposited. For the Al_2O_3 and Li_2O/Al_2O_3 catalysts there were no significant differences in activity and selectivity detected, compared to the measurements without oxygen. For the CeO_x containing catalysts an increase in CO formation is recorded. For the CeO_x/Al_2O_3 catalyst a CO selectivity up to 50% was found and for the $Li_2O/CeO_x/Al_2O_3$ catalyst a selectivity to CO of 21% was found.

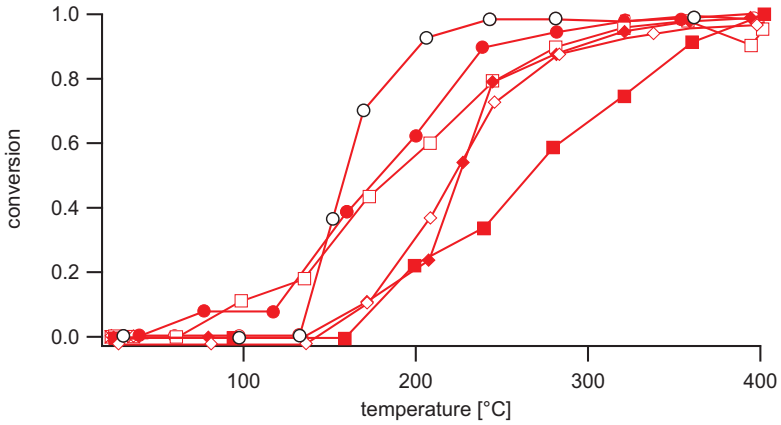

Figure 5.1: Ethanol conversion vs temperature. Ethanol dehydrogenation in the absence of oxygen. First heating stage(closed symbols), cooling stage (open symbols). ○Cu/Al_2O_3, ◊ $Cu/Li_2O/Al_2O_3$, □ $Cu/CeO_x/Al_2O_3$

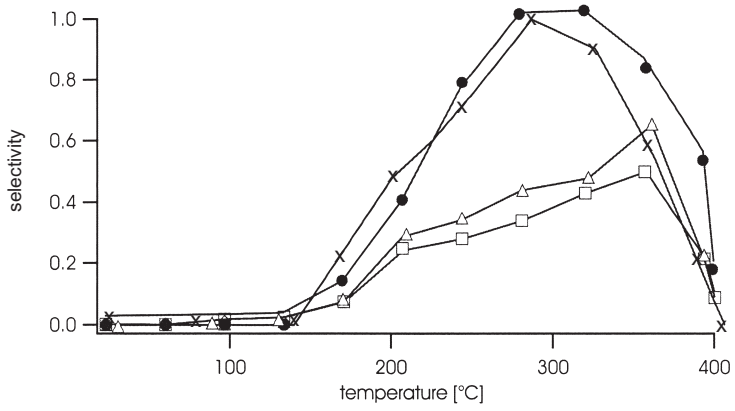

Figure 5.2: Ethylene oxide selectivity vs temperature. First heating stage in ethanol-only flow. x Cu/Al_2O_3, ●$Cu/Li_2O/Al_2O_3$, □ $Cu/CeO_x/Al_2O_3$, △ $Cu/Li_2O/CeO_x/Al_2O_3$

Table 5.2: conversion and selectivities of ethanol dehydrogenation on the used supports. TC = total conversion, S_1 = selectivity toward diethyl ether, S_2 = selectivity toward ethylene, S_3 = selectivity toward CO

Catalyst	Temperature (°C)	TC	S_1	S_2	S_3
Al_2O_3	200	38	92	8	0
	250	70	86	14	0
	300	100	30	70	0
	400	100	0	100	0
CeO_x/Al_2O_3	200	5	80	20	0
	250	30	13	84	3
	300	100	3	69	28
	400	100	0	64	36
Li_2O/Al_2O_3	200	0	0	0	0
	250	31	84	16	0
	300	72	69	31	0
	350	90	67	33	0
	400	100	50	50	0
$Li_2O/CeO_x/Al_2O_3$	200	10	80	20	0
	250	37	81	19	0
	300	100	45	50	5
	400	100	34	58	8

5.3.3 Ethanol dehydrogenation on copper based catalysts

In the dehydrogenation of ethanol there is a significant difference between the first heating cycle and the following cycles, which in the figures and tables are represented by the first cooling cycle. The results of the 2^{nd} and further heating/cooling stages resemble that of the 1^{st} cooling cycle. The ethanol conversion as a function of reaction temperature of the first heating step is presented in figure 5.1. The Cu/Al_2O_3 catalyst being the most active. The conversion starts at 140°C and reaches maximum conversion around 225°C. The $Cu/Li_2O/Al_2O_3$ is slightly less active and the conversion on both CeO_x containing catalysts starts around 170°C and reaches 100% conversion above 300°C.

In figure 5.2 the selectivities towards ethylene oxide are presented. Clearly, the Cu/Al_2O_3 and $Cu/Li_2O/Al_2O_3$ are much more selective towards ethylene oxide. The

selectivity towards ethylene oxide decreases at high temperatures and then mainly ethylene is formed. When the gas flow was bubbled through a diluted NaOH solution glycol was produced, which is further evidence that the output gas flow contained ethylene oxide. Also minor quantities of acetaldehyde and diethyl ether are formed. ForOn the $Cu/CeO_x/Al_2O_3$ catalyst mainly CO is formed next to ethylene oxide. In the following cooling cycle the conversion of ethanol is slightly improved for the $Cu/CeO_x/Al_2O_3$ and Cu/Al_2O_3 catalysts. For the $Cu/Li_2O/Al_2O_3$ catalyst the conversion is about the same. In terms of selectivity there is a big change compared to the first heating cycle. The results are summarized in table 5.3. The greatest difference is the absence of ethylene oxide formation. It is only formed in trace amounts. Compared to the results of the support oxides only, the addition of copper results in more ethylene oxide formation.

Table 5.3: Selectivities for Cu based catalysts in ethanol-only flow. First cooling cycle. S_1 = ethylene, S_2 = acetaldehyde, S_3 = diethyl ether, S_4 = CO, S_5 = ethylene oxide

Catalyst	Temperature (°C)	S_1	S_2	S_3	S_4	S_5
Cu/Al_2O_3	200	-	-	100	-	-
	300	80	15	5	-	-
	400	100	-	-	-	-
$Cu/CeO_x/Al_2O_3$	200	-	-	-	100	-
	300	25	5	-	70	-
	400	46	10	8	36	-
$Cu/Li_2O/Al_2O_3$	200	-	-	-	-	-
	300	60	12	12	-	15
	400	70	15	10	-	5

5.3.4 Ethanol oxidation on copper based catalysts

For an ethanol/oxygen mixture of 1 the results are shown in figure 5.3 and the selectivities in table 5.4. Contrary to the measurements without oxygen in the reaction flow, all the heating and cooling steps show the same behavior. The Cu/Al_2O_3 and $Cu/Li_2O/Al_2O_3$ catalysts show ethanol conversion from 140°C. For the $Cu/Li_2O/Al_2O_3$ catalyst the O_2 conversion starts at higher temperature. $Cu/CeO_x/Al_2O_3$ is the least active catalyst with ethanol and oxygen conversion starting at 200°C. The $Cu/Li_2O/Al_2O_3$ and Cu/Al_2O_3 catalyst show a high selectivity toward ethylene oxide at

Table 5.4: Selectivities for Cu based catalysts in an ethanol/O_2 mixture of 1, S_1 = ethylene, S_2 = acetaldehyde, S_3 = diethyl ether, S_4 = CO, S_5 = ethylene oxide

Catalyst	Temperature (°C)	S_1	S_2	S_3	S_4	S_5
Cu/Al_2O_3	200	-	-	-	30	70
	300	15	15	-	20	50
	400	100	-	-	-	-
$Cu/CeO_x/Al_2O_3$	200	-	-	-	-	-
	300	20	5	-	55	20
	400	60	-	-	40	-
$Cu/Li_2O/Al_2O_3$	200	-	-	-	10	90
	300	60	12	12	-	15
	400	90	2	2	2	4

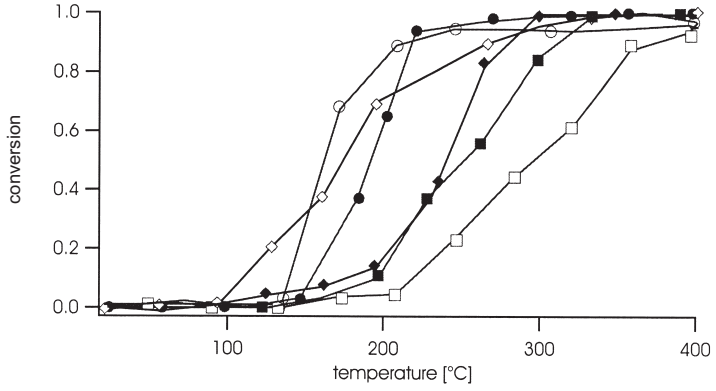

Figure 5.3: Ethanol conversion vs temperature. Ethanol/O_2 mixture of 1. First heating stage(closed symbols), cooling stage (open symbols). ○Cu/Al_2O_3, ◊ $Cu/Li_2O/Al_2O_3$, □ $Cu/CeO_x/Al_2O_3$

Table 5.5: Selectivities for Ag based catalysts in ethanol-only flow. First cooling cycle S_1 = ethylene, S_2 = acetaldehyde, S_3 = diethyl ether, S_4 = CO, S_5 = ethylene oxide

Catalyst	Temperature (°C)	S_1	S_2	S_3	S_4	S_5
Ag/Al_2O_3	200	-	-	100	-	-
	300	40	-	40	20	-
	400	100	-	-	-	-
$Ag/CeO_x/Al_2O_3$	200	75	-	-	20	5
	300	64	-	-	36	-
	400	32	-	-	68	-
$Ag/Li_2O/Al_2O_3$	200	60	-	30	-	10
	300	90	-	-	5	5
	400	100	-	-	-	-

temperatures up to 300°C. The selectivity is then shifted towards ethylene and CO. The $Cu/CeO_x/Al_2O_3$ catalyst show higher selectivity towards CO and much lower selectivity towards ethylene oxide. On all catalysts some acetaldehyde and diethylether are formed with selectivities under 10%. No H_2 is detected but only H_2O. The Li_2O containing catalyst was also checked for stability. At temperatures of 240°C no deactivation was found for 72 hours.

5.3.5 Ethanol dehydrogenation on silver based catalysts

The silver based catalysts are already active at a temperature of about 100°C as shown in figure 5.4, which is a significantly lower temperature than for the copper based catalysts. For the $Ag/Li_2O/Al_2O_3$ catalyst the onset of ethanol conversion is about 50°C higher than for the Ag/Al_2O_3 and $Ag/CeO_x/Al_2O_3$ catalysts. The selectivities are also quite different from the copper based catalyst as can be seen in table 5.5. No differences between first heating stage and the other stages are found. Very little ethylene oxide is produced. Instead only ethylene and CO are formed. When Li_2O is added to the Ag/Al_2O_3 catalyst, some improvement to the ethylene oxide selectivity is obtained but it remains under 10%. For the $Ag/CeO_x/Al_2O_3$ catalyst the selectivity shifts to CO as the temperature is increased. Also increasing amounts of H_2 are detected. On the Ag/Al_2O_3 some diethylether is formed at low temperatures and some traces of acetaldehyde are detected.

5.3.6 Ethanol oxidation on silver based catalysts

In figure 5.5 the results of an ethanol/O_2 mixture of 1 are presented. The Ag/Al_2O_3 and $Ag/CeO_x/Al_2O_3$ catalyst show ethanol conversion from 100°C onward. The $Ag/Li_2O/Al_2O_3$ catalyst is less active and show an onset temperature of 150°C for the ethanol conversion. For the Ag/Al_2O_3 catalyst the O_2 conversion is similar to the ethanol conversion. This is not the case for the $Ag/Li_2O/Al_2O_3$ catalyst, where the ethanol conversion starts at 120°C and the O_2 conversion starts from 190°C. In this temperature region mainly ethylene oxide is formed. Compared to the ethanol-only flow the activity is not greatly influenced by the oxygen, but the effect of O_2 on the selectivity is much greater; as shown in table 5.6. For the Ag/Al_2O_3 catalyst the effect of adding oxygen results in an increased CO production at the expense of diethyl ether, but also a decrease in ethylene. For the $Ag/CeO_x/\gamma\text{-}Al_2O_3$ catalyst ethylene and CO remain still the two important products, but also other products are formed. For the $Ag/Li_2O/Al_2O_3$ catalyst there is a big shift from ethylene production towards ethylene oxide when O_2 is added, also diethyl ether is formed at high temperatures. The Li_2O containing catalyst was also checked for stability. At temperatures of 240°C no deactivation was found for 72 hours.

Table 5.6: Selectivities for Ag based catalyats in an ethanol/O_2 mixture of 1, S_1 = ethylene, S_2 = acetaldehyde, S_3 = diethyl ether, S_4 = CO, S_5 = ethylene oxide

Catalyst	Temperature (°C)	S_1	S_2	S_3	S_4	S_5
Ag/Al_2O_3	200	-	10	-	85	5
	300	60	5	-	40	-
	400	16	-	-	84	-
$Ag/CeO_x/Al_2O_3$	200	12	5	33	39	10
	300	24	-	13	54	9
	400	43	-	-	57	-
$Ag/Li_2O/Al_2O_3$	200	-	4	-	-	96
	300	23	-	21	-	54
	400	28	-	38	4	30

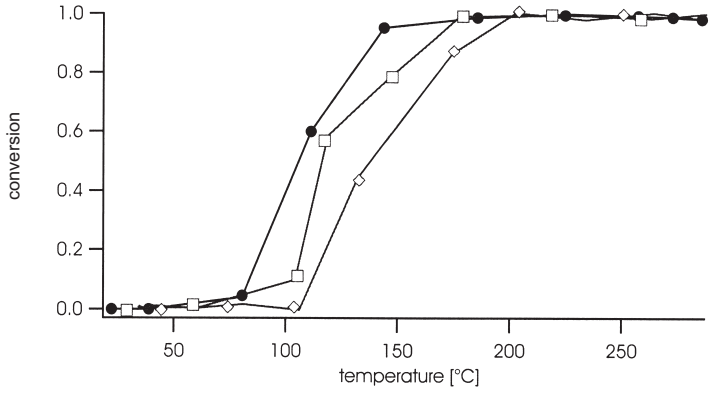

Figure 5.4: Ethanol conversion vs temperature. Ethanol dehydrogenation in the absence of oxygen. First cooling stage. ●Ag/Al_2O_3, ◊ $Ag/Li_2O/Al_2O_3$, □ $Ag/CeO_x/Al_2O_3$

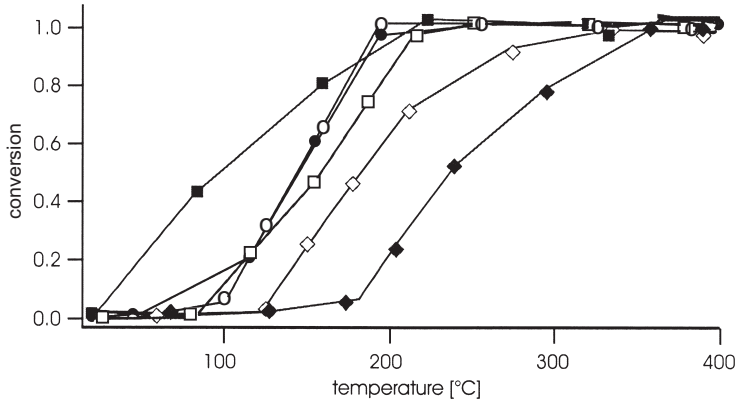

Figure 5.5: Ethanol conversion (open symbols) and oxygen conversion (closed symbols) vs temperature. The ethanol/O_2 ratio = 1 ○Ag/Al_2O_3, ◊ $Ag/Li_2O/Al_2O_3$, □ $Ag/CeO_x/Al_2O_3$

5.4 Discussion

5.4.1 Activity of copper based catalysts

In agreement with literature [10, 23] the Al_2O_3 support only converts the ethanol into diethyl ether and ethylene and a small amount of acetaldehyde. When copper is added to the support, the Cu/Al_2O_3 catalyst also produces ethylene oxide which is not observed on the Al_2O_3 support. To our knowledge production of ethylene oxide from ethanol in an single reaction has not been reported before in literature. Apparently, the presence of copper nanoparticles is necessary for the formation of ethylene oxide. In another study of our group similar results were found for gold based catalysts [15]. At high temperatures the selectivity resembles that of the support only. However, the addition of copper has a positive effect on the ethanol conversion. Clearly, the copper particles are capable of partly oxidizing the ethanol. Especially when CeO_x is added their is a great improvement in selectivity to carbon monoxide, while much less ethylene oxide is formed. This can be attributed to the capability of CeO_x in supplying oxygen to the copper particles. When no oxygen is added to the gas flow, the formation of ethylene oxide is only observed in the first heating cycle and not in the following cycles. This is probably caused by carbon deposition on the active copper sites. After all the stages indeed carbon deposition was found. Heating the catalyst in an O_2 flow produced CO_2. When this was followed by a pretreatment in hydrogen the catalyst was regenerated. When O_2 was added to the gas flow no deactivation or carbon deposition was found, hence O_2 prevents carbon deposition on the sites that are active in converting ethanol into ethylene oxide. The addition of Li_2O to the γ-Al_2O_3 support results in a great decrease of the conversion, possibly by affecting the strong acidic sites of the alumina [10, 14, 19]. The addition of lithia to the Cu/Al_2O_3 catalyst does not result in significant changes in conversion and selectivity. Apparently, in the presence of copper nanoparticles the reaction pathways are not dependent on the acidic sites of alumina.

5.4.2 Activity of silver based catalysts

The addition of silver to the γ-Al_2O_3 support improves the activity but does not change the selectivity to diethyl ether and ethylene much. These products diethyl ether and ethylene are mainly the result of the catalytic activity of γ-Al_2O_3. A difference between Ag/Al_2O_3 and Al_2O_3 catalyst is the formation of small quantities of CO, showing some oxidation capabilities of the silver particles, which is enhanced by

the addition of CeO_x. Addition of Li_2O shifts the selectivity towards ethylene but also introduces another product: ethylene oxide. This is probably caused by the effect of Li_2O on the acidic sites of the alumina, and so increasing the relative weight of the reaction pathway to ethylene oxide. This is in particular the case with O_2 present in the gas flow, where addition of Li_2O results in a great increase in selectivity towards ethylene oxide. Apparently for the silver particles both the presence of Li_2O and O_2 are needed to obtain a good selectivity to ethylene oxide. This is in contrast to copper and gold based catalysts [15] which can also produce ethylene oxide in the absence of oxygen, because those metals have greater oxidation capabilities.

5.5 Conclusions

Results show that both silver and copper nanoparticles are active in oxidation, dehydrogenation and dehydration of ethanol. They are also capable of converting ethanol directly into ethylene oxide. Indications of multiple catalytic reaction centers and multiple pathways are found. The presence of O_2 is very important to prevent carbon deposition for copper based catalysts. For the silver based catalysts O_2 is also needed to improve the selectivity towards CO. For the silver based catalysts the presence of both Li_2O and O_2 is needed to obtain a good selectivity to ethylene oxide.

5.6 Acknowledgements

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6

Direct conversion of ethanol into ethylene oxide on gold based catalysts

Results are presented concerning the behavior of alumina supported gold catalysts and the effects of addition of Li_2O and CeO_x on the oxidation, dehydrogenation and dehydration reactions of ethanol. Pure alumina mainly acts as an acidic catalyst and produces diethyl ether and ethylene. Gold particles play an important role in converting ethanol into ethylene oxide and acetaldehyde. Addition of Li_2O influences the selectivity by suppressing the formation of diethyl ether and ethylene. With the $Au/Li_2O/Al_2O_3$ catalysts a high selectivity toward ethylene oxide can be obtained. The influence of the oxygen concentration in the gas flow is investigated. It is suggested that at low concentrations the role of oxygen is mainly to prevent coke formation on the catalytic surface.

6.1 Introduction

Due to the diminishing availability and the high prices of crude oil and natural gas much attention is paid to the use of alternative resources. Ethanol is receiving much interest since it has a reasonably high hydrogen content and it can be produced by the fermentation of corn and other renewable resources. One of the possible options is the production of hydrogen by partial oxidation or steam reforming [1]. In addition, selective oxidation of ethanol may also be important for the synthesis of chemical intermediates in the manufacture of high-tonnage commodities [**?**, 2]. Ethanol can be converted to e.g. acetaldehyde, ethylene, ethyl acetate, ethane, carbon monoxide/hydrogen and as this paper will show, ethylene oxide, in addition to its total oxidation products carbon dioxide and water. Ethanol is commercially used for ethylene oxide production in a two step reaction by the Chemtex corporation. First ethanol is converted to ethylene after which the ethylene is oxidized with O_2 over a silver based catalyst. This paper reportrs a direct, one step, conversion of ethanol into ethylene oxide.

Ethanol is also a simple probe molecule for the investigation of surface reactions on metals [1, 3, 4] and oxides [5, 6]. On most surfaces the ethanol molecules first dissociate to ethoxy species. These ethoxy species are further oxidized to acetaldehyde or dehydrated to ethylene. On metal surfaces acetaldehyde either desorbs or decomposes to CO and methane [7]. In addtion, coupling and bimolecular hydrogenation reactions may occur resulting in the production of higher hydrocarbons such as diethyl ether, ethyl acetate, acetic acid or ketene [**?**, 8, 9].

Highly dispersed gold on metal oxides supports exhibits an extraordinarily high activity in various low-temperature oxidation reactions [10–16]. The gold particle size is of huge importance for high oxidation activity. This motivated us to investigate the reactions of various alcohols on γ-Al_2O_3 supported gold catalysts. In a recent publication results have been presented of non-oxidative ethanol dehydrogenation of ethanol on silica supported gold catalysts [17]. It was shown that the gold particle size affects the activity just as was reported for oxidation reactions. This effect of particle size was attributed to the role of step sites on the gold surface. Previously reported results show that ceria has a promoting effect on the activity of Au/Al_2O_3 in CO and other oxidation reactions [15, 18]. It was argued that the active oxygen was supplied by the ceria. In addition, it was reported that the size of the ceria particles has a great influence on the activity of the catalyst [19]. A detailed study of Gluhoi et al. [20, 21] on the effects of addition of (earth) alkali metals to a Au/Al_2O_3

catalyst revealed that the main role of the (earth) alkali metals is to stabilize the gold nanoparticles. Hence, the alkali metal acts as a structural promoter. The oxidative dehydrogenation of ethanol to acetaldehyde is known to be catalyzed by materials possessing strong base sites such as Li_2O [22].

In this study we investigated the behavior of Au/Al_2O_3 catalysts in the dehydrogenation, dehydration and oxidation reactions of ethanol. In addition, the promoting effects of Li_2O and CeO_x have been investigated. CeO_x is an active oxide for the oxidation of CO to CO_2 and for making H_2 from ethanol by reforming [23]. Earlier work concerning the oxidation of methanol revealed that addition of Li_2O has a great effect on the acidic sites of γ-Al_2O_3 and so influences the selectivity to products which are not formed on these acidic sites [24]. Similar results have been found for copper and silver based catalysts [**?**, 25].

6.2 Experimental

6.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x) and Li_2O on alumina were prepared by pore volume impregnation of γ-Al_2O_3 (BASF, de Meern) with the corresponding nitrates. After calcination at 350°C these oxides were used as support for the Au particles. The prepared mixed oxides had an intended Ce/Al and Li/Al ratio of 1/15. The gold catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent. The appropriate amount of $HAuCl_4$.3aq (99.999% Aldrich chemicals) was added to a suspension of purified water containing γ-Al_2O_3 or the mixed oxide. The intended M/Al ratio was 1/75 (M= Au). This ratio of 1:75 is equal to 0.53at% M and results in 5wt% for gold. The temperature was kept at 80 °C allowing urea (p.a.,Acros) to decompose ensuring a slow increase of pH. When a pH of around 8-8.5 was reached the slurry was filtrated and washed thoroughly with water and dried overnight at 80 °C. The catalysts were thoroughly ground to ensure that the macroscopic particle size was around 200μm for all the catalysts used in this study.

6.2.2 Catalyst characterization

The metal loading was verified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Varian Vista-MPX. For that purpose a small fraction of the

catalyst was dissolved in diluted aqua regia. X-ray diffraction measurements were done using a Philips Goniometer PW 1050/25 diffractometer equipped with a PW Cu 2103/00 X-ray tube operating at 50kV an 40mA. The average particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [26].

6.2.3 Activity measurements

Activity tests of the catalysts were performed in a micro reactor system. A oxygen flow balanced in argon was bubbled through a vessel containing absolute ethanol. This gas flow was led to a lab scale flow reactor made from quartz with a internal diameter of 1 cm. In the reactor the catalyst was placed on a quartz bed. The amount of catalyst used was 0.2g for the Au/γ-Al_2O_3 catalysts. For catalysts containing CeO_x and/or Li_2O the amount of catalyst was adjusted in such a way that the amount of gold was similar for all the catalysts with and without additives. Prior to activity experiments the catalysts were reduced with H_2 (4 vol% in Ar) at 400 °C for 2 hours.

Two different ratios of oxygen/ethanol were used for the oxidation of ethanol: 1:1, and one with excess oxygen (6:1). For the decomposition reaction a argon flow was bubbled through the vessel. Typically, a total gas flow of 40ml^{-1}(GHSV $\approx$ 2500h^{-1})was maintained. The effluent stream was analyzed on-line by a gas chromatograph (HP 8590) with a CTR1 column (Alltech) containing a porous polymer mixture, an activated molecular sieve and a Hayesep Q column (Alltech). All possible reaction products were calibrated by injecting a dilute solution directly into the GC or in case of gases as ethylene and ethylene oxide the gas flow from lecture bottles was diluted with argon and led to the GC. Mass spectrometry confirmed that the analysis of the reaction products by gas chromatography was correct. To distinguish the different components the relative intensity ratios of masses 15,29,43,44,45 were used.

The experiments were carried out at atmospheric pressure. Each reaction test consisted of at least two heating-cooling cycles from room temperature up to 400°C, with a rate of 2°C/min in order to monitor possible catalyst deactivation and hysteresis processes.

6.3 Results

6.3.1 Characterization

The average gold particle size of the fresh catalysts could not be determined by XRD because the size of the particles was below the detection limit of 3nm. The results of the characterization of the catalysts after the reaction (CO oxidation) are shown in table 6.1. The catalysts without additives contain small particles of 3-4nm. With ceria and Li_2O added the average particle size is lower than the detection limit. HRTEM data of comparable catalysts have been published in earlier papers of our group [20, 21]. The actual metal loading was almost equal to the intended metal loading. In addition, we have checked the catalysts for the Li and Ce contents with ICP-OES. These measurements showed that the appropriate amount of Li and/or Ce was deposited on the catalysts.

6.3.2 Activity of catalyst supports without gold particles

In table 6.2 the results of the supports without gold, in the dehydrogenation of ethanol in the absence of oxygen are presented. The most active support is γ-Al_2O_3 without additive. The main products are the dehydration products diethyl ether and ethylene. Also some trace amounts of acetaldehyde are found at temperatures up to 300°C. Addition of ceria to the γ-Al_2O_3 results in formation of CO at temperatures above 300°C, at the expense of diethyl ether and ethylene. Addition of Li_2O to the alumina catalysts lowers the ethanol conversion compared to the γ-Al_2O_3 only catalyst. Addition of Li_2O results in a higher selectivity towards ethylene. No acetaldehyde is found. The catalyst which contains both Li_2O and CeO_x show a behavior with the typical characteristics of both Li_2O/Al_2O_3 and CeO_x/Al_2O_3 catalysts.

Table 6.1: Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Average particle size (nm)
Au/Al_2O_3	4.6±0.1	4.3±0.1
$Au/CeO_x/Al_2O_3$	4.1±0.1	<3.0
$Au/Li_2O/Al_2O_3$	4.5±0.3	3.2±0.1
$Au/CeO_x/Li_2O/Al_2O_3$	4.0±0.2	<3.0

Table 6.2: conversion and selectivities of ethanol dehydrogenation on the used supports. TC = total conversion(%), S_1 = selectivity toward diethyl ether, S_2 = selectivity toward ethylene, S_3 = selectivity toward CO

Catalyst	Temperature (°C)	TC	S_1	S_2	S_3
Al_2O_3	200	38	92	8	0
	250	70	86	14	0
	300	100	30	70	0
	400	100	0	100	0
CeO_x/Al_2O_3	200	5	80	20	0
	250	30	13	84	3
	300	100	3	69	28
	400	100	0	64	36
Li_2O/Al_2O_3	200	0	0	0	0
	250	31	84	16	0
	300	72	69	31	0
	350	90	67	33	0
	400	100	50	50	0
$Li_2O/CeO_x/Al_2O_3$	200	10	80	20	0
	250	37	81	19	0
	300	100	45	50	5
	400	100	34	58	8

In addition, measurements have been performed for an ethanol/O_2 mixture of 1 . For the Al_2O_3 and Li_2O/Al_2O_3 catalysts there were no significant differences in activity and selectivity compared to the measurements without oxygen. On the CeO_x containing catalyst some increase in CO formation is recorded, up to 50% selectivity for the CeO_x/Al_2O_3 catalyst and 21% selectivity for the $Li_2O/CeO_x/Al_2O_3$ catalyst.

6.3.3 Ethanol dehydrogenation reaction in the absence of O_2 over the gold based catalysts

In the dehydrogenation of ethanol in the absence of O_2 over the Au-based catalyst there is a significant difference between the first heating stage and the following cycles, which in the figures are represented by the first cooling stage. The results of the 2^{nd} and further heating/cooling stages resemble that of the 1^{st} cooling stage,

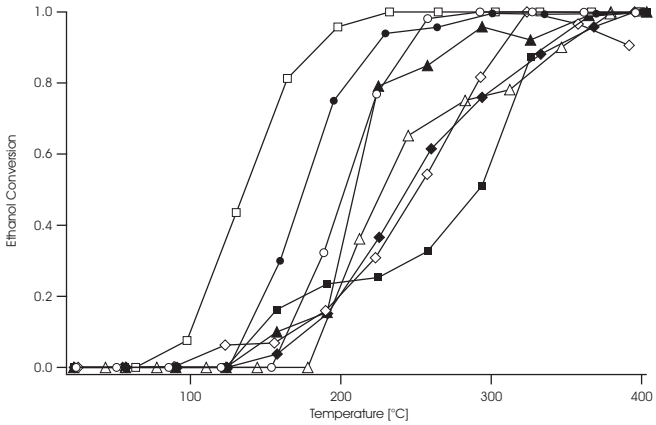

Figure 6.1: Ethanol conversion vs temperature in the absence of oxygen. First heating stage(closed symbols), cooling stage(open symbols). ○ Au/Al_2O_3, ◇ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

which is depicted in the figures shown. The ethanol conversion as a function of reaction temperature is presented in figure 6.1. In the first heating stage (closed symbols) the ethanol conversion starts at 150-200 °C, the Au/Al_2O_3 catalyst being the most active and the $Au/CeO_x/Al_2O_3$ the least active catalyst with a onset temperature of 250 °C. However, in the first cooling stage and the following cycles(open symbols) the behavior is different. The catalyst which shows the largest difference is the $Au/CeO_x/Al_2O_3$ catalyst, with a temperature of 50% conversion of 130 °C compared to 300 °C in the first heating stage. The performance of the other catalysts are similar to the first heating stage.

The product selectivities are presented in figures 6.2,6.3,6.4,6.5. The detected products were ethylene, acetaldehyde, diethyl ether, hydrogen and ethylene oxide. No CO_2, H_2O and CO were detected. Only in the first heating stage ethylene oxide is produced, see figure 6.2. Selectivities up to 50% to ethylene oxide were obtained at 300 °C for the Li_2O containing catalysts. The Au/Al_2O_3 and $Au/CeO_x/Al_2O_3$ catalyst produced ethylene oxide at lower temperatures around 250°C but only with low selectivity. In the following cooling and heating stages no ethylene oxide was produced.

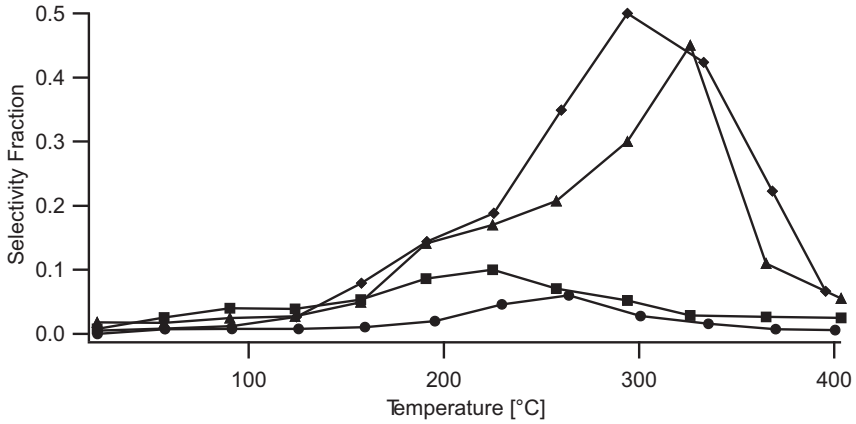

Figure 6.2: Ethylene oxide selectivity vs temperature in the absence of oxygen. First heating stage. ● Au/Al_2O_3, ♦ $Au/Li_2O/Al_2O_3$, ■ $Au/CeO_x/Al_2O_3$ and ▲ $Au/Li_2O/CeO_x/Al_2O_3$

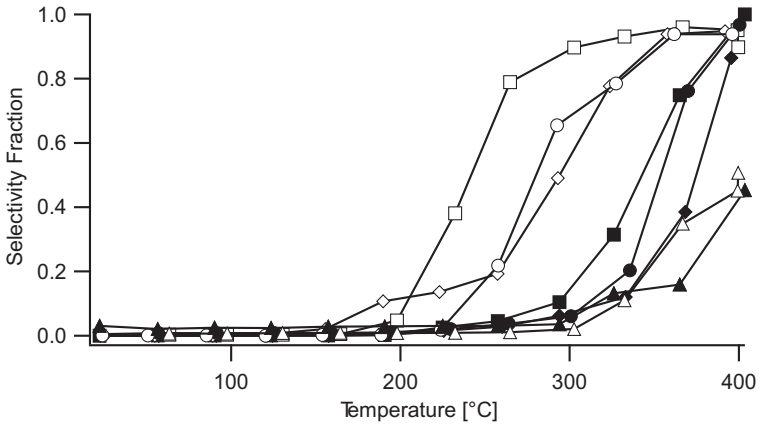

Figure 6.3: Ethylene selectivity vs temperature in the absence of oxygen. First heating stage(closed symbols), cooling stage(open symbols). ○ Au/Al_2O_3, ◇ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

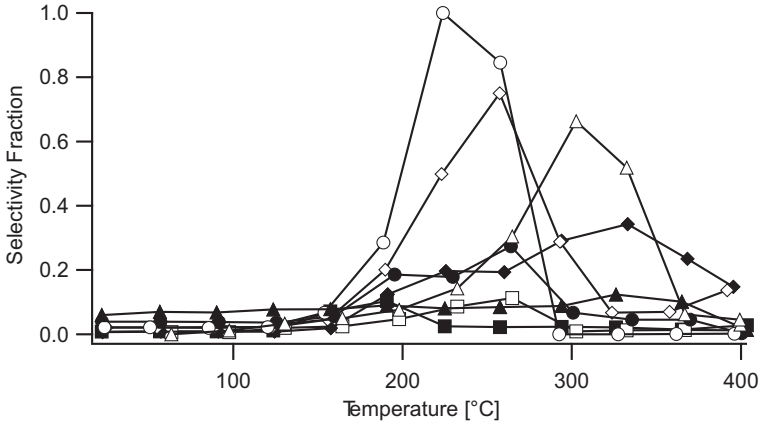

Figure 6.4: Diethyl ether selectivity vs temperature in the absence of oxygen. First heating stage(closed symbols), cooling stage(open symbols). ○ Au/Al_2O_3, ◊ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

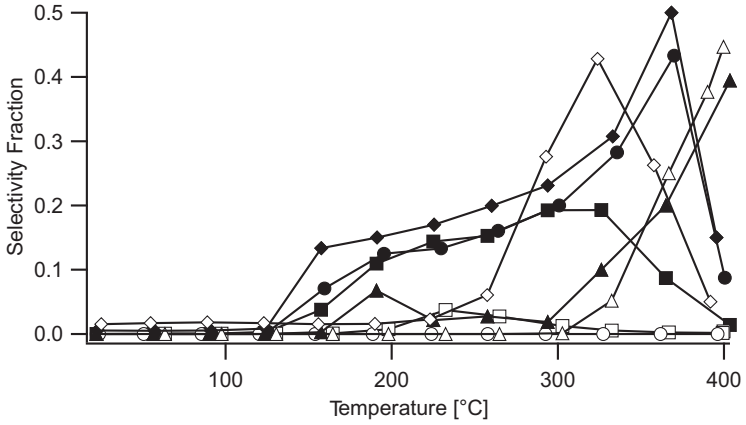

Figure 6.5: Aldehyde selectivity vs temperature in an ethanol/O_2 mixture of 1. First heating stage(closed symbols), cooling stage(open symbols). ○ Au/Al_2O_3, ◊ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

Ethylene formation is presented in figure 6.3. In the first heating step the formation of ethylene starts at 320 °C. The selectivity increases to 100 %} at 400 °C on the Au/Al_2O_3 and $Au/CeO_x/Al_2O_3$ catalysts. On the $Au/Li_2O/Al_2O_3$ catalyst the formation starts at 350 °C and reached a maximum selectivity of 85 % at 400 °C. The $Au/Li_2O/CeO_x/Al_2O_3$ catalyst shows the least ethylene formation. The formation of ethylene starts at 350 °C and has a maximum selectivity of 45 % at 400 °C. In the cooling step and the following cycles the ethylene formation already starts at the lower temperatures of 200-250 °C, with the exception of the $Au/Li_2O/CeO_x/Al_2O_3$ catalyst which shows low selectivty to ethylene at higher temperatures.

The formation of acetaldehyde is shown in figure 6.5. In the first heating step acetaldehyde formation starts at 160 °C on all catalysts except for the $Au/Li_2O/CeO_x/Al_2O_3$ catalyst. On that catalyst acetaldehyde is not observed below 300 °C. At the same temperature the Au/Al_2O_3 and $Au/Li_2O/Al_2O_3$ catalysts show a second increase in acetaldehyde formation. This increase was not observed for $Au/CeO_x/Al_2O_3$ which has the lowest selectivity for acetaldehyde. In the cooling step and following cycles only the Li_2O containing catalysts show significant selectivities to acetaldehyde at high temperatures.

On the Au/Al_2O_3 and $Au/CeO_x/Al_2O_3$ only traces of acetaldehyde were detected. In the first heating step there is a low selectivity to diethyl ether on the Au/Al_2O_3 and $Au/CeO_x/Al_2O_3$ catalysts between 200-300 °C as shown in figure 6.4. In the following steps much higher selectivities were obtained. The Au/Al_2O_3 and $Au/Li_2O/Al_2O_3$ showed maximum selectivity between 200-270 °C. The $Au/Li_2O/CeO_x/Al_2O_3$ catalysts showed a maximum selectivity at 300 °C.

6.3.4 Ethanol oxidation in an ethanol/O_2 mixture of 1.

The conversion of ethanol using an ethanol/O_2 mixture of 1 is presented in figure 6.7. In the first heating step the reaction starts at higher temperatures compared to the cooling step. In the subsequent cycles the behavior is rather similar to that of the first cooling step. The conversion starts at 100 °C and reaches a maximum at about 275 °C. The $Au/Li_2O/Al_2O_3$ shows the best activity. The oxygen conversion (shown in figure 6.6) starts at higher temperatures compared to the ethanol conversion. The addition of Li_2O or CeO_x lowers the temperature of oxygen uptake by 50 °C. The oxygen conversion starts at 150 °C and reaches a maximum conversion at 250 °C for the CeO_x containing catalysts, and for Au/Al_2O_3 and $Au/Li_2O/Al_2O_3$ the oxygen conversion reaches maximum conversion at 350 °C.

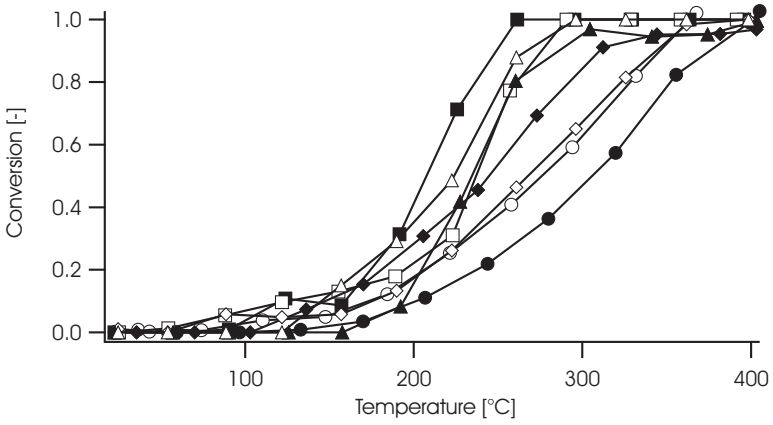

Figure 6.6: Oxygen conversion vs temperature in an ethanol/O_2 mixture of 1. First heating stage(closed symbols), cooling stage(open symbols). ○ Au/Al_2O_3, ◊ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

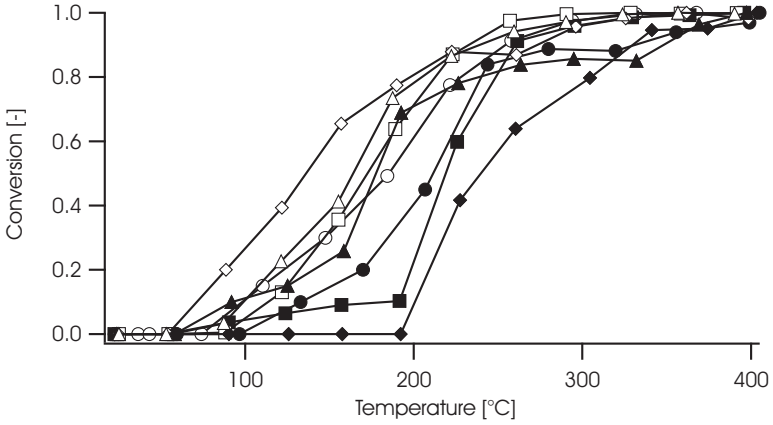

Figure 6.7: Ethanol conversion vs temperature in an ethanol/O_2 mixture of 1. First heating stage(closed symbols), cooling stage(open symbols). ○ Au/Al_2O_3, ◊ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

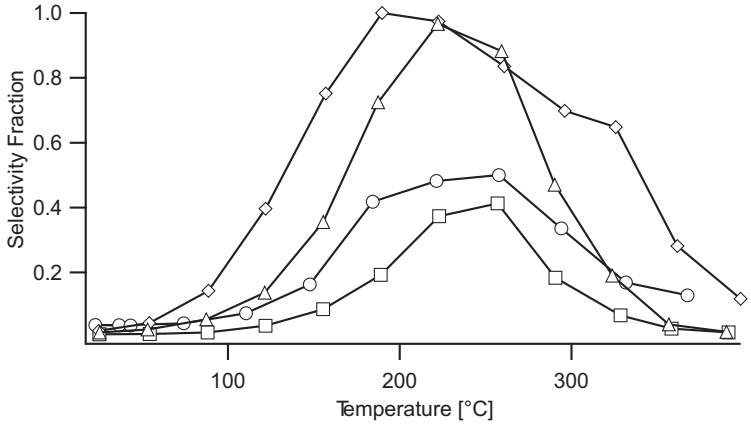

Figure 6.8: ethylene oxide selectivity vs temperature in an ethanol/O_2 mixture of 1. First cooling stage(open symbols). ○ Au/Al_2O_3, ◊ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

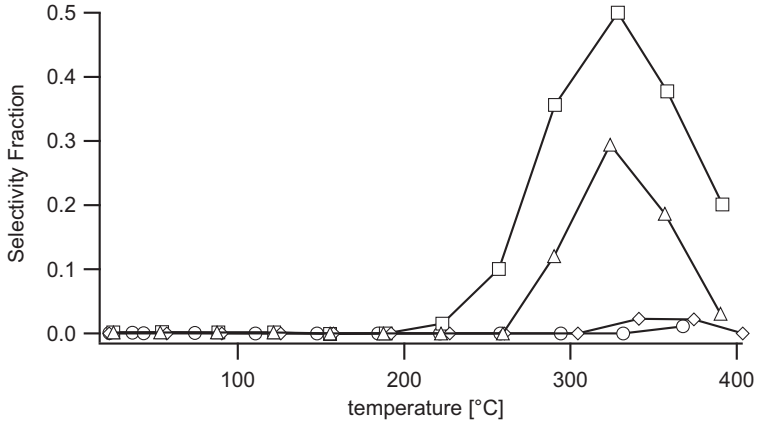

Figure 6.9: Diethyl ether selectivity vs temperature in an ethanol/O_2 mixture of 1. First cooling stage(open symbols). ○ Au/Al_2O_3, ◊ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

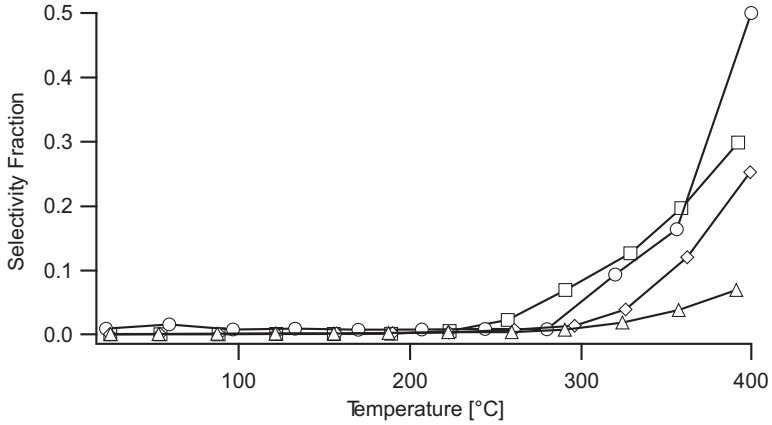

Figure 6.10: ethylene selectivity vs temperature in an ethanol/O_2 mixture of 1. First heating stage(closed symbols), cooling stage(open symbols). ○ Au/Al_2O_3, ◊ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

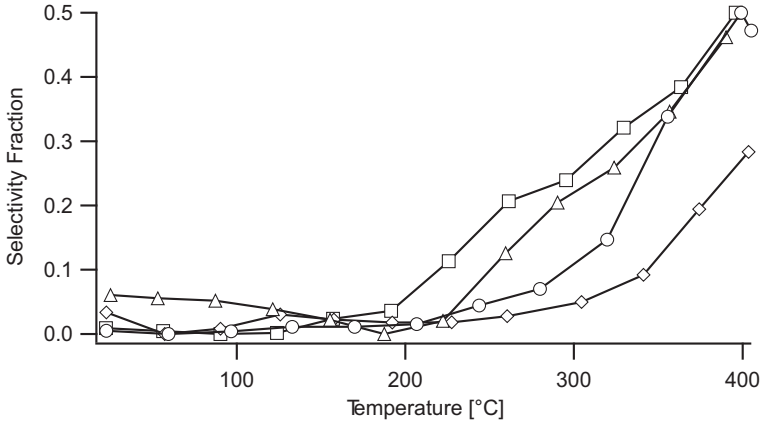

Figure 6.11: CO_2 selectivity vs temperature in an ethanol/O_2 mixture of 1. First cooling stage(open symbols). ○ Au/Al_2O_3, ◊ $Au/Li_2O/Al_2O_3$, □ $Au/CeO_x/Al_2O_3$ and △ $Au/Li_2O/CeO_x/Al_2O_3$

At temperatures between 100 °C and 250°C the main product is ethylene oxide, as can be seen in figure 6.8. The catalyst with the best performance in ethylene oxide formation is $Au/Li_2O/Al_2O_3$. A selectivity to ethylene oxide of 88% is reached. With this catalyst also traces of the combination product of ethylene oxide and ethanol (ethoxy-ethanol) were detected. When the gas flow was bubbled through a diluted NaOH solution glycol was produced, which is further evidence that the output gas flow contained ethylene oxide. At temperatures between 250-400 °C diethylether was formed over the two CeO_x containing catalysts, as shown in figure 6.9. The addition of ceria to the Au/Al_2O_3 catalyst also results in more ethane formation (not shown). Also ethylene and CO_2 and traces of CO were formed as shown in figures 6.10 and 6.11. Au/Al_2O_3 showed the highest selectivity to CO_2 production and the $Au/CeO_x/Al_2O_3$ catalyst showed the highest selectivity to ethylene formation.

6.3.5 Ethanol oxidation in excess oxygen

The results of ethanol oxidation over Au/Al_2O_3 in excess oxygen (ethanol/O_2 =1/6) are presented in figures 6.12 and 6.13. Ethanol conversion starts from 150 °C and a sharp increase in conversion is observed at 200 °C. At this temperature also the O_2 conversion and the CO_2 production start. At temperatures above 300 °C ethanol is mainly ethanol oxidized to CO_2. The ethylene oxide production can be assigned to the activity of gold as the γ-Al_2O_3 support produces no ethylene oxide. Addition of Li_2O shown in figures 6.12 and 6.14 increases the ethanol conversion between 50 and 200 °C. The main product in this temperature region is ethylene oxide while no oxygen is consumed. The oxygen conversion is similar to the Au/Al_2O_3 catalyst as is the CO_2 production.

In figures 6.12 and 6.15 the effect of addition of CeO_x is shown. The onset of both ethanol and oxygen conversion is shifted to 175 °C. CO_2 production already starts at 200 °C. At temperatures up to 250 °C the intermediate products ethylene oxide, diethyl ether and ethylene are detected.

The results of addition of both Li_2O and CeO_x are presented in figures 6.12 and 6.16. The $Au/Li_2O/CeO_x/Al_2O_3$ catalyst shows an activity similar to the Au/Al_2O_3 catalyst when the ethanol and oxygen conversion are considered. The selectivity to ethylene oxide is increased and similar to the
$Au/Li_2O/Al_2O_3$ catalyst, but with a lower ethanol conversion. At temperatures above 350 °C some ethylene is formed.

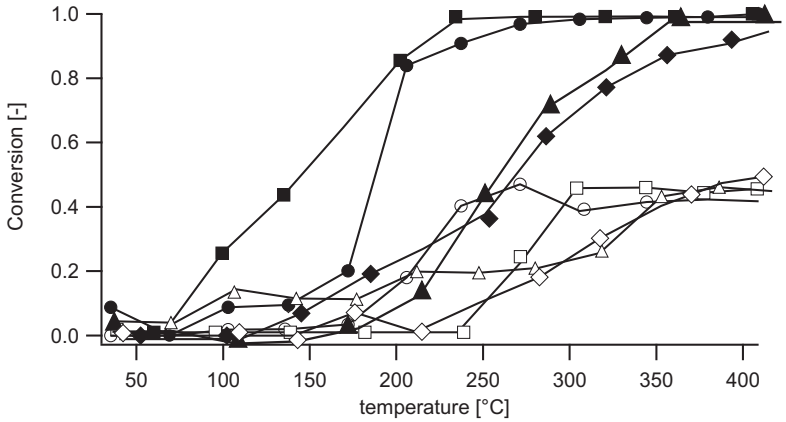

Figure 6.12: Ethanol conversion in excess oxygen. Ethanol conversion(closed symbols) and oxygen conversion (open symbols) vs temperature, First cooling stage. ▲ Au/Al_2O_3, ● $Au/CeO_x/Al_2O_3$, ■ $Au/Li_2O/Al_2O_3$ and ♦ $Au/Li_2O/CeO_x/Al_2O_3$

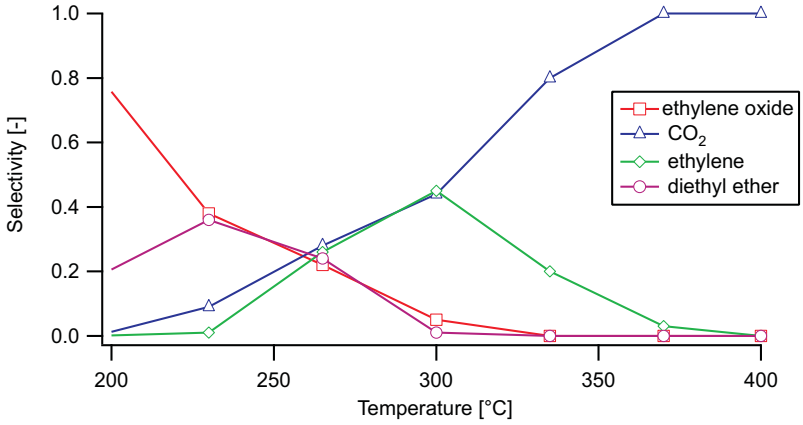

Figure 6.13: Ethanol conversion in excess oxygen. Selectivity vs temperature on Au/Al_2O_3 catalyst. First cooling stage

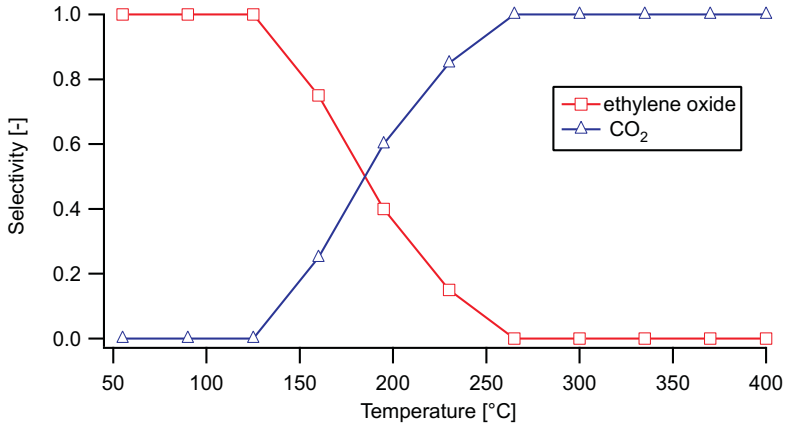

Figure 6.14: Ethanol conversion in excess oxygen. Selectivity vs temperature on $Au/Li_2O/Al_2O_3$ catalyst. First cooling stage

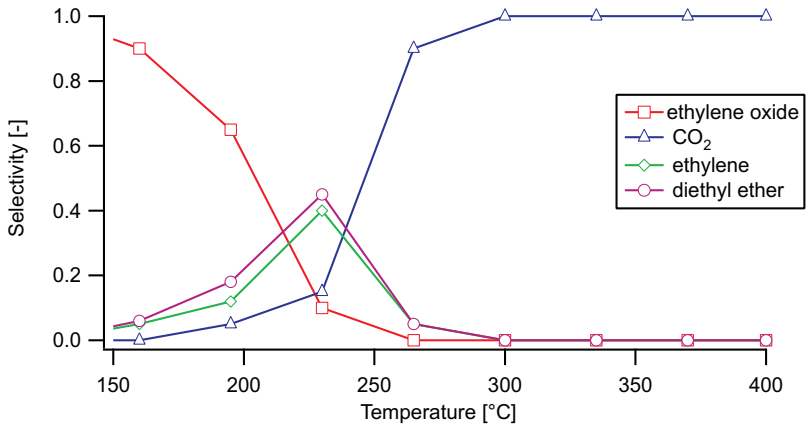

Figure 6.15: Ethanol conversion in with excess oxygen. Selectivity vs temperature on $Au/CeO_x/Al_2O_3$ catalyst. First cooling stage

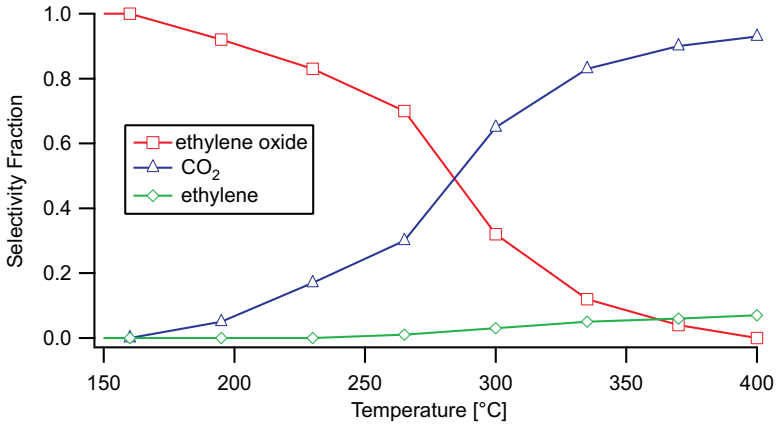

Figure 6.16: Ethanol conversion in excess oxygen. Selectivity vs temperature on $Au/Li_2O/CeO_x/Al_2O_3$ catalyst. First cooling stage

6.4 Discussion

6.4.1 Activity and selectivity of Au/Al_2O_3

In agreement with literature data [27, 28] the Al_2O_3 support only converts ethanol into diethyl ether and ethylene and a small amount of acetaldehyde. When gold is added to the support, the Au/Al_2O_3 catalyst also produces ethylene oxide which is not observed on the Al_2O_3 support. To our knowledge ethylene oxide production from ethanol in a single reaction has not been reported earlier in the literature. Apparently, the presence of gold nanoparticles is necessary for the formation of ethylene oxide. At temperatures above 325 °C, the addition of gold enhances the formation of acetaldehyde at the expense of ethylene but apparently, a second pathway via the gold particles contributes at temperatures above 325 °C. In the cooling stage and consecutive cycles no difference between Au/Al_2O_3 catalyst and the Al_2O_3 support is observed. This can be explained by carbon deposition during the first heating stage, which deactivates the active gold sites. Indications that carbon deposition is taking place are the color change. The catalysts turns black after the first heating stage. When this black catalyst is used in a temperature programmed oxidation experiment with O_2, CO_2 is formed and the color is restored to the original purple color and also

the activity is restored. Similar results have been found for copper based catalysts [**?**]. The formation of diethyl-ether and ethylene is not affected by the carbon deposition. The formation of these products is catalyzed by the acid sites of alumina [27], which apparently are not affected by the carbon deposition. Addition of a small amount of oxygen does not influence the onset temperature of the ethanol conversion, but the oxygen prevents the carbon deposition as no deactivation is noticed in the ethylene oxide formation. The decrease of ethylene oxide at temperatures above 250°C is probably due to the further oxidation to CO_2.

6.4.2 Addition of Li_2O to the Au/Al_2O_3 catalyst

Addition of Li_2O has indeed a significant effect on the selectivity in the dehydrogenation of ethanol. The selectivity to ethylene oxide is increased, whereas the selectivities to the acid-catalyzed products ethylene and diethyl ether are decreased. This can be attributed to the absence of strong acidic sites on the Li_2O/Al_2O_3. In the consecutive cooling and heating steps on the Li_2O containing catalyst there is still acetaldehyde formation, although the temperature is shifted compared to the first heating step. As the Li_2O/Al_2O_3 only catalyst does not show any acetaldehyde formation, this activity can be attributed to gold. Apparently as the formation of ethylene oxide is hindered by carbon deposition on the active gold sites, a second type of active gold sites is still active in acetaldehyde formation. This is in agreement with earlier findings that Li_2O acts as a structural promoter for the Au/Al_2O_3 catalyst [25, 29]. Addition of oxygen prevents the blocking of the active sites by carbon deposition and enhances the selectivity to ethylene oxide. Above 300°C the ethylene oxide is further oxidized to CO_2 and ethylene. The same is valid for the measurements with excess oxygen.

6.4.3 Addition of CeO_x to the Au/Al_2O_3 catalyst

The addition of ceria has not a great influence on the catalyst activity in the first heating step of the ethanol dehydrogenation. The temperature shift in diethyl ether formation suggests that this reaction no longer takes place at the acid sites of the alumina but on the ceria surface. In the consecutive cooling and heating stages the addition of ceria results in a slight improvement of the activity. The CeO_x cannot prevent coke formation on the active gold sites. The addition of ceria improves the oxygen conversion in the measurements with oxygen, whereas in the absence of oxygen, the $Au/CeO_x/Al_2O_3$ shows the worst acetaldehyde selectivity. Possibly, the ceria

increases the acetaldehyde formation by providing oxygen to the ethoxy-species on the gold, which is further oxidized to acetaldehyde. This also applies for the measurements with excess oxygen where the CeO_x containing catalyst shows the highest oxygen conversion and CO_2 formation from 200 °C.

6.4.4 Addition of both CeO_x and Li_2O

Addition of both CeO_x and Li_2O results in a typical behavior of a mixed catalyst. By addition of Li_2O the strong acid sites of Al_2O_3 are reduced, which explains the low selectivity to ethylene shown in figure 6.3. The effect of CeO_x is apparent in the formation of the coupling product diethyl ether. In the measurements with oxygen the $Au/Li_2O/CeO_x/Al_2O_3$ catalyst shows the lowest onset temperature, but the highest temperature of 100% conversion. This also applies for the experiments with excess oxygen where on this catalyst no maximum conversion is reached up to 400 °C.

6.4.5 Comparison of ethylene oxide formation with silver and copper based catalysts

Recently, ethanol dehydrogenation and oxidation have been studied on copper and silver based catalysts [25]. On the copper based catalysts formation of ethylene oxide was found in the first heating stage in ethanol dehydrogenation. In the following cooling stage much less ethylene oxide was formed, as also was observed for the gold based catalyst. On the silver based catalysts no ethylene oxide was detected in the ethanol dehydrogenation reaction. Measurements with an ethanol/O_2 ratio of 1 show ethylene oxide formation on all three metal based catalysts. In table 6.3 some results of the catalysts with the best performance in ethylene oxide production are presented. In all cases the best selectivity is achieved with the Li_2O containing catalysts. The $Au/Li_2O/Al_2O_3$ catalysts show the highest ethanol conversion with good selectivity to ethylene oxide at 200°C. At temperatures of 300°C the selectivity to ethylene oxide is the highest on the $Au/Li_2O/Al_2O_3$ catalyst. At higher temperatures the selectivity to ethylene oxide drops on all catalysts but remains the highest for $Ag/Li_2O/Al_2O_3$.

With all three metal based catalysts, the most promising results are found when Li_2O is added, suggesting that the role of Li_2O is very important in the conversion of ethanol into ethylene oxide. The copper and gold based catalysts show some similarity in reactivity and selectivity. The gold based catalyst is the most selective to ethylene oxide. Both show a maximum selectivity around 200°C. At higher temperat-

ures the selectivity decreases with increasing temperature, as ethylene, CO and CO_2 are formed. The silver based catalyst also shows high selectivity to ethylene oxide at 200°C but at lower conversion than the gold based catalyst. At temperatures of 400°C the selectivity to ethylene oxide remains at higher levels, less CO, ethylene and no CO_2 are formed. The silver based catalyst also differs from the copper and gold based catalyst as in ethanol dehydrogenation no ethylene oxide is formed.

6.4.6 Role of gold, lithium, cerium and oxygen

The results presented do not result in a complete picture of the mechanism of ethylene oxide formation from ethanol, but some annotations can be made. As ethylene oxide formation is only observed in the presence of gold-nanoparticles, it can be concluded that the gold-particles contain active sites needed for the formation of ethylene oxide. When an ethanol-only flow is used, these sites are deactivated by carbon deposition. The selectivity then shifts to formation of acetaldehyde, which is not observed on the bare support. Hence, most probably, another active site is present on the gold which is active in formation of acetaldehyde, and this site is not affected by carbon deposition.

It is unlikely that the formation of ethylene oxide is the result of a reaction of ethanol on the gold particles with oxygen from the support as the addition of ceria, which is very capable of supplying oxygen [**?**, 18] would then increase the formation of ethylene oxide and just the opposite is found.

We believe that the ethylene oxide if formed directly from the ethanol, by abstracting hydrogen. In experiments with varying contact time no indications were found of any intermediates. Also when an ethylene/O_2 flow was used no ethylene oxide was detected. The only carbon containing products were CO and CO_2.

Addition of Li-species results in a great increase in selectivity to ethylene oxide. This promoting effect of lithium may be twofold. First, lithium can act as a structural promoter by influencing the shape and size, and thus the active sites, of the gold particles [20]. Second, it lowers the activity of the alumina support by influencing the acidic sites of the alumina. In this way it favors the reaction pathway in which the gold-nanoparticles are involved.

For the role of oxygen we have made the following observations: Ethanol conversion and ethylene oxide formation start at lower temperature than O_2 conversion. Secondly, we found no apparent relation between O_2 conversion and ethylene oxide formation. These observations led us to believe that the main role of oxygen is to

Table 6.3: comparison of conversion of ethanol and selectivities into ethylene oxide in an ethanol/O_2 mixture of 1.

Catalyst	Temperature (°C)	Conversion	Selectivity
$Au/Li_2O/Al_2O_3$	200	80	95
	300	90	71
	400	100	10
$Ag/Li_2O/Al_2O_3$	200	58	96
	300	90	54
	400	100	30
$Cu/Li_2O/Al_2O_3$	200	70	90
	300	92	15
	400	100	4

prevent coke formation. In the measurements with high O_2 content almost no ethylene oxide is formed, but the ethanol is further oxidized mainly to CO_2. Hence, a low concentrating of oxygen is important for a high ethylene oxide selectivity.

6.5 Conclusions

Gold based catalysts are active in ethanol dehydrogenation, oxidation and dehydratation. In a gas flow with a low O_2 concentration a high selectivity to ethylene oxide can be obtained. The presence of O_2 is very important to prevent carbon deposition. With the best performing catalyst, $Au/Li_2O/Al_2O_3$ a selectivity to ethylene oxide up to 88% is obtained. By improving the oxygen uptake, ceria makes oxygen available to the catalytic reaction sites. No indications are found of a combinatorial effect of Li_2O and CeO_x in these reactions.

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7

Dehydrogenation, dehydration and oxidation of propanol over gold based catalysts

Our recent results concerning the formation of ethylene oxide from ethanol on gold based catalysts [1] motivated us the investigate the possibility of converting 1-propanol and/or 2-propanol directly to propylene oxide. In this exploratory study we found that gold based catalysts are capable of converting propanol to acetone and propylene. Minute traces of propylene oxide are found. It is suggested that the conversion of 1-propanol to acetone and 2-propanol is proceeding via a propylene oxide intermediate.

7.1 Introduction

The major industrial application of propylene oxide (about 65%) is as a monomer for the production of polyether polyols for use in making polyurethane plastics. Propylene oxide is also used in the production of propylene glycol (using about 30% of propylene oxide) and propylene glycols ethers(about 5%).

Industrial production of propylene oxide is currently performed in three different processes, which are complex and have economic and environmental disadvantages [2]. The chlorohydrin method uses chlorine and propylene. The two other methods use hydroperoxide and a second chemical (iso-butene or benzene) which results in production of the coproducts styrene or tert-butyl alcohol. Using Enichem TS-1 technology [3, 4] DOW and BASF propylene is oxidized with hydrogen peroxide tot propylene oxide and water. In this process no side products other than water are formed.

As the current production methods have disadvantages, much research is devoted to the development of new catalysts and new processes to improve the propylene oxide production. One of the methods under study is the use of gold-titania catalysts, which are potentially attractive since propylene oxide is produced out of propylene, hydrogen and oxygen in a single reactor under mild conditions. Unfortunately, however, the conversion levels (2%) are too low for industrial application [5].

Our recent results concerning the oxidation of ethanol on gold based catalysts, which show a high selectivity towards production of ethylene oxide [**?**, 1] motivated us the investigate the possibility of converting 1-propanol and/or 2-propanol directly to propylene oxide. The catalytic decomposition of 2-propanol is also a simple probe reaction to study surface reactions on metals and investigate the acid-base properties of metal oxides. The decomposition occurs in two parallel reactions, dehydration on acidic sites to give propylene and dehydration to give acetone on basic or redox sites [6].

In this exploratory study we investigated the performance of gold based catalysts in the dehydrogenation, dehydration and oxidation reactions of 1-propanol and 2-propanol. In addition, the effects of adding Li_2O and CeO_x have been investigated in line with the large effects found with the addition of Li_2O and CeO_x on methanol [7] and ethanol [1] oxidation over Au/Al_2O_3. We did not include the $Au/Li_2O/CeO_x/Al_2O_3$ catalyst in this study, as the addition of both CeO_x and Li_2O

to the gold based catalyst did not show any synergistic effects in methanol and ethanol oxidation [1, 7].

Previously reported results show that ceria has a promoting effect on the activity of the Au/Al_2O_3 catalyst in CO oxidation [8, 9]. It was argued that the active oxygen was supplied by the ceria, rather than from the gas phase. In addition, it was reported that the size of the ceria particles has a great influence on the activity of the catalyst [10]. A detailed study of Gluhoi et al. [11, 12] on the effects of addition of (earth) alkali metals to a Au/Al_2O_3 catalyst revealed that the main role of the (earth) alkali metals is to stabilize the gold particles i.e that of a structural promoter in the investigated reactions. Comparable results have been found for copper and silver based catalysts [13]. The oxidative dehydrogenation of ethanol to acetaldehyde is known to be catalyzed by materials possessing strong base sites such as Li_2O [14].

7.2 Experimental

7.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x) and Li_2O on alumina were prepared by pore volume impregnation of γ-Al_2O_3 (BASF, de Meern) with the corresponding nitrates. After calcination at 350°C these oxides were used as support for the Au particles. The prepared mixed oxides had an intended Ce/Al and Li/Al ratio of 1/15. The gold catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent. The appropriate amount of $HAuCl_4$.3aq (99.999% Aldrich chemicals) was added to a suspension of purified water containing γ-Al_2O_3 or the mixed oxide. The intended M/Al ratio was 1/75 (M= Au). This ratio of 1:75 is equal to 0.53at% M and results in 5wt% for gold. The temperature was kept at 80 °C allowing urea (p.a.,Acros) to decompose ensuring a slow increase of pH. When a pH of around 8-8.5 was reached the slurry was filtrated and washed thoroughly with water and dried overnight at 80 °C. The catalysts were thoroughly ground to ensure that the macroscopic particle size was around 200μm for all the catalysts used in this study.

7.2.2 Catalyst characterization

The metal loading was verified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Varian Vista-MPX. For that purpose a small fraction of the

catalyst was dissolved in diluted aqua regia. X-ray diffraction measurements were done using a Philips Goniometer PW 1050/25 diffractometer equipped with a PW Cu 2103/00 X-ray tube operating at 50kV a 40mA. The average particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [15].

7.2.3 Activity measurements

Prior to activity experiments the catalysts were reduced with H_2 (4 vol% in Ar) at 400 °C for 2 hours. Activity tests of the catalysts were performed in a micro reactor system. An oxygen flow balanced in argon was bubbled through a vessel containing absolute propanol. The oxygen/propanol ratio used was: 1:1, For the decomposition reaction a argon flow was bubbled through the vessel. Typically a total gas flow of $40ml^{-1}$(GHSV $\approx$ $2500h^{-1}$)was maintained. The effluent stream was analyzed online by a gas chromatograph (HP 8590) with a CTR1 column (Alltech) containing a porous polymer mixture and an activated molecular sieve and a Hayesep Q column (Alltech). The experiments were carried out at atmospheric pressure. Each measurement contains of multiple temperature programmed cycles of heating and cooling, with a rate of 2/°C min. The detected products were also confirmed with as mass spectrometer.

7.3 Results

7.3.1 Characterization

The average particle size of the fresh catalysts could not be determined by XRD because the size of the particles was below the detection limit of 3nm. The results of the characterization of the catalysts after the reaction are shown in table 7.1. The catalysts without additives contain small particles of 3-4nm. With ceria and Li_2O added the average particle size is lower than the detection limit (3nm). HRTEM data of comparable catalysts have been published in earlier papers of our group [11, 12]. The actual metal loading was almost equal to the intended metal loading. In addition, we have checked the catalysts for the Li and Ce contents with ICP-OES. These measurements showed that the appropriate amount of Li and/or Ce was deposited on the catalysts.

Table 7.1: Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Average particle size (nm)
Au/Al_2O_3	4.6±0.1	4.3±0.1
$Au/CeO_x/Al_2O_3$	4.1±0.1	<3.0
$Au/Li_2O/Al_2O_3$	4.5±0.3	3.2±0.1

7.3.2 Activity of catalyst supports without gold particles

The results of the activity of the used supports are summarized in tables 7.2 and table 7.3. Addition of oxygen to the feed does not result in a significant change in the activity and selectivity. For all used supports only acetone and propylene are formed, with small differences in selectivity. At temperatures of 400°C propylene is the only product. When 2-propanol is used temperatures of 100% conversion are lower compared to the oxidation of 1-propanol.

Table 7.2: conversion and selectivities of 1-propanol oxidation on the used supports. The propanol/O_2 ratio is 1. TC = total conversion, S_1 = selectivity toward propylene, S_2 = selectivity toward acetone

Catalyst	Temperature (°C)	TC	S_1	S_2
Al_2O_3	200	8	50	50
	250	80	75	25
	300	100	25	75
	400	100	0	100
CeO_x/Al_2O_3	200	5	80	20
	250	30	85	15
	300	100	69	28
	400	100	0	100
Li_2O/Al_2O_3	200	0	0	0
	250	31	84	16
	300	72	69	31
	350	90	39	61
	400	100	0	100

Table 7.3: conversion and selectivities of 2-propanol oxidation on the used supports. The propanol/O_2 ratio is 1. TC = total conversion, S_1 = selectivity toward propylene, S_2 = selectivity toward acetone

Catalyst	Temperature (°C)	TC	S_1	S_2
Al_2O_3	200	15	70	30
	250	90	64	36
	300	100	20	80
	400	100	0	100
CeO_x/Al_2O_3	200	5	80	20
	250	30	85	15
	300	100	0	100
	400	100	0	100
Li_2O/Al_2O_3	200	0	0	0
	250	0	0	0
	300	60	67	33
	350	90	33	67
	400	100	0	100

7.3.3 Propanol dehydrogenation in the absence of O_2 on gold based catalysts

The results of the measurements of 1-propanol or 2-propanol in the absence of O_2 are presented in tables 7.4 and 7.5. On the gold based catalysts no significant differences are found compared to the bare supports. Propylene and acetone are the only formed products. Hence gold nanoparticles are not active in propanol dehydrogenation.

7.3.4 1-Propanol oxidation in a propanol/O_2 mixture of 1

In figure 7.1 the activity and selectivity of the Au/Al_2O_3 catalysts is presented. Compared to the bare support γ-Al_2O_3 the onset temperature of the conversion is lowered by 30°C and the selectivity toward acetone is increased. No other products are formed. On the $Au/CeO_x/Al_2O_3$ catalyst 1-propanol is converted to propylene, acetone and CO_2 as shown in figure 7.2. The addition of gold to the ceria/Al_2O_3 supports results in formation of CO_2 at temperatures above 350°C. In figure 7.3 the results are depicted of the $Au/Li_2O/Al_2O_3$ catalyst.

Table 7.4: conversion and selectivities of 1-propanol dehydrogenation. TC = total conversion, S_1 = selectivity toward propylene, S_2 = selectivity toward acetone

Catalyst	Temperature (°C)	TC	S_1	S_2
Au/Al_2O_3	200	16	50	50
	250	85	76	24
	300	100	40	60
	400	100	5	95
$Au/CeO_x/Al_2O_3$	200	10	80	20
	250	40	88	10
	300	100	65	35
	400	100	0	100
$Au/Li_2O/Al_2O_3$	200	1	100	0
	250	37	86	14
	300	73	75	25
	350	92	49	51
	400	100	2	98

Table 7.5: conversion and selectivities of 2-propanol dehydrogenation. TC = total conversion, S_1 = selectivity toward propylene, S_2 = selectivity toward acetone

Catalyst	Temperature (°C)	TC	S_1	S_2
Au/Al_2O_3	200	10	80	20
	250	80	82	18
	300	100	50	50
	400	100	5	95
$Au/CeO_x/Al_2O_3$	200	15	53	47
	250	47	73	27
	300	100	62	38
	400	100	0	100
$Au/Li_2O/Al_2O_3$	200	1	100	0
	250	30	87	13
	300	70	79	21
	350	88	53	47
	400	100	1	99

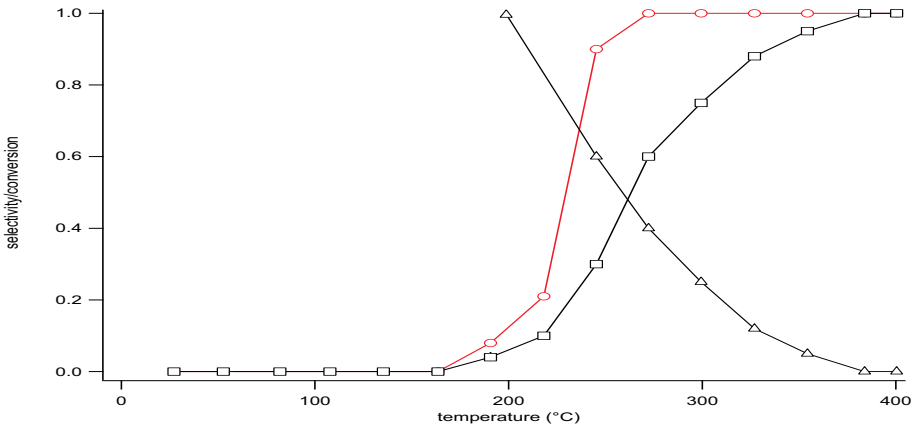

Figure 7.1: conversion of 1-propanol in the presence of oxygen over Au/Al_2O_3 catalyst. The propanol/O_2 ratio = 1. ○ propanol conversion, △ acetone selectivity, □ propylene selectivity

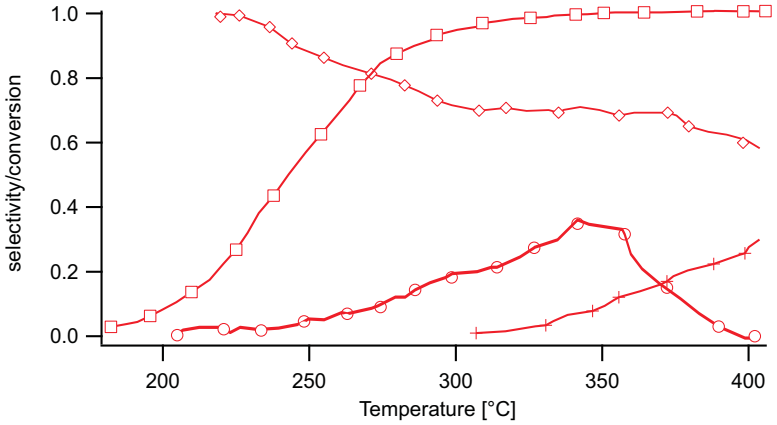

Figure 7.2: conversion of 1-propanol in the presence of oxygen over $Au/CeO_x/Al_2O_3$ catalyst. The propanol/O_2 ratio = 1. □ propanol conversion, ○ acetone selectivity, ◊ propylene selectivity, + CO_2 selectivity

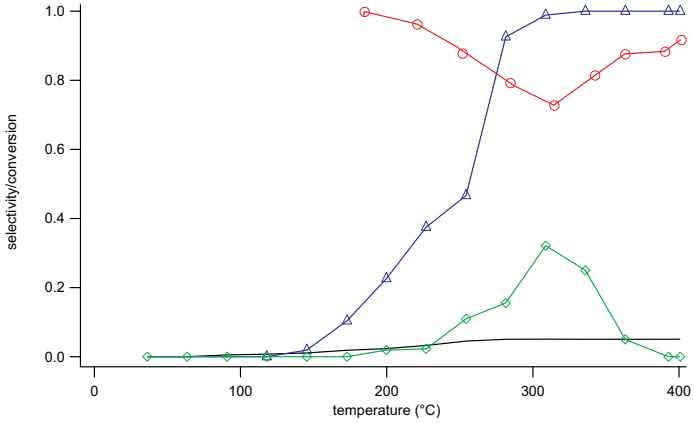

Figure 7.3: conversion of 1-propanol in the presence of oxygen over $Au/Li_2O/Al_2O_3$ catalyst. The propanol/O_2 ratio = 1. △ propanol conversion, ◊ acetone selectivity, ○ propylene selectivity, - selectivity other trace amounts

The major products are acetone and propylene, but also some other products are found in minute quantities. Among these are propylene oxide (maximum selectivity of 1%), 2-propanol and oxetane.

7.3.5 2-propanol oxidation in a propanol/O_2 mixture of 1

The oxidation of 2-propanol on the gold based catalysts results in the products acetone, propylene and carbon dioxide. The results are summarized in table 7.6. No indications of other products are found. CO_2 is only formed on the ceria containing catalyst, comparable to the results of 1-propanol.

Table 7.6: conversion and selectivities of 2-propanol oxidation on gold based catalysts. The 2-propanol/O_2 ratio is 1. TC = total conversion, S_1 = selectivity toward propylene, S_2 = selectivity toward acetone, S_3 = selectivity toward CO_2

Catalyst	Temperature (°C)	TC	S_1	S_2	S_3
Au/Al_2O_3	200	0	0	0	0
	250	40	80	20	0
	300	100	62	38	0
	400	100	0	100	0
$Au/CeO_x/Al_2O_3$	200	5	60	40	0
	250	55	64	27	9
	300	100	40	50	10
	400	100	0	70	30
$Au/Li_2O/Al_2O_3$	200	0	0	0	0
	250	25	88	12	0
	300	66	79	21	0
	350	86	56	44	0
	400	100	0	100	0

7.3.6 Discussion

Almost all measured catalysts show comparable activities and selectivities. The conversion of propanol starts around 200°C and two products are formed: propylene and acetone. These two products should be formed in two parallel reactions: dehydration on acidic sites to give propylene and dehydration to give acetone on basic or redox sites. Addition of lithia to the γ-Al_2O_3 support improves the selectivity to acetone a little bit. However this effect of lithia is much smaller than observed for methanol and ethanol [1, 7]. Probably, the conversion of propanol is much less dependent of the acidic sites of the alumina than methanol and ethanol. Addition of gold nanoparticles results in a higher conversion only when oxygen is present in the gas flow. In the absence of oxygen no effect of gold addition to the supports is detected. This suggests that the gold particles play a important role in activating the oxygen which can react on the interface with propanol adsorbed at the support as C_3H_7O species. Addition of ceria in the presence of oxygen improves the oxidation strength of the catalyst resulting in total oxidation of propanol to CO_2. As the CeO_x/Al_2O_3 catalyst does not show CO_2 formation also the gold particles play a role in the oxidation. Ceria

is known to be capable of providing oxygen to gold nanoparticles to assist in oxidation reactions [12]. The most interesting results have been obtained for the 1-propanol oxidation in the presence of O_2 over the $Au/Li_2O/Al_2O_3$ catalyst. With this catalyst the predominant products are acetone and propylene but also some minute amounts of other products are found, including propylene oxide and 2-propanol. It shows that this catalyst is active in the isomerization of 1-propanol to 2-propanol. It is suggested that the found propylene oxide and 2-propanol products are intermediate products in the conversion of 1-propanol to acetone.

7.3.7 Conclusions

In this exploratory study is found that gold based catalysts are capable of converting propanol to acetone and propylene. No other products with high selectivities are found. The addition of CeO_x and Li_2O does not result in major improvement in the investigated reaction. Indications are found that the conversion of 1-propanol to acetone is proceeding via a propylene oxide intermediate. Further investigation is necessary to be able to discriminate between primary and secondary oxidation products and gain clear insight into the mechanism of propanol oxidation to various products.

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8
General discussion

8.1 Particle size effects

From literature is it clear that gold deposited as nanoparticles on a transition metal oxide support is a very active catalyst in contrast to bulk gold which does not show any catalytic activity. The question arises if this particle size effect is unique gold or can a similar effect be found for the related metals copper and silver? Using a γ-Al_2O_3 support very stable gold nanoparticles can be obtained by using 2 additives: 1) a transition metal oxide or ceria and 2) an (earth)alkali oxide such as Li_2O [3, 4]. In this thesis it is investigated if this approach also works for silver and copper. In chapter 3 a comparison could be made between the results presented and literature data from Gang et al. [1,2]. It became apparent also with the use of silver there is a particle size effect. In the case of ammonia oxidation it is not in the sense of enhanced activity but in a change in selectivity. The nanoparticles are much more selective towards N_2. Hence the size of the silver particles is important for the catalytic activity. When copper is used deposited as nanoparticles comparable activity and selectivity is found, but with a much lower copper loading 1.5wt% in stead of 5wt%. Hence for both metals: copper and silver it can be stated that the size of the particles is important in

the catalaytic capabilities in ammonia oxidation. For the other investigated oxidation and dehrogenation reactions no comparison with literature data was possible. In the studies in oxidation and dehydrogenation of methanol (chapter 4) and ethanol (in chapter 5 and chapter 6) all three used metals showed remarkable activity in these reactions. The reactivity of copper and gold are the most alike, where catalysis on the silver nanoparticles seem to follow a different reaction path. In the preferential CO oxidation, methanol oxidation and also the ethanol oxidation different selectivity was found for the silver based catalysts than for the copper and gold based catalysts. In chapter 2 two particle sizes of deposited silver were used in the preferential oxidation of O_2. In this reaction it became apparent that the small particles ($<$3nm) were more active than the bigger particles (8-9nm). A second conclusion that could be drawn was that on larger particles the influence of the used additives was much less compared to the effect of the additives on the smaller particles. This supports the idea that the interaction of additives and the nanoparticles is very important for the catalytic activity.

8.2 Effect of Li_2O

Gluhoi et al. [3, 4] investigated the role of alkali(earth) metal oxides on gold nanoparticles. The results reveal that for the investigated reaction, propene oxidation, the additives were not responsible for the higher catalytic activity but act as structural promoters by increasing the concentration of active sites, by preventing sintering of the gold nanoparticles. This effect was also found in the investigated reactions of this thesis. Addition of Li_2O not only lead to smaller gold particles but also on the silver and copper based catalysts a smaller average particle size was found when Li_2O was added. When alkali oxides (such as lithium oxide) are used with an acidic γ-Al_2O_3 support, the tetrahedral Lewis Al^{3+} sites are poisoned by the alkali metal [5]. The effect is strongly dependent on the amount of alkali metal [6] and on the atomic radii [7]. The used amount of Li_2O oxide in this thesis was about 10wt%, so we can regard the amount as a larger amount of lithium oxide. Hence it can be assumed that all the acidic sites of the alumina are poisoned. This effect is indeed found in the oxidation of the alcohols in chapter 4,5,6 and chapter 7. When Li_2O was added the formation of products which is dependent on the presence of acidic sites are greatly decreased. This in combination with a low O_2 concentration in the gas flow makes it possible to get high selectivities of interesting (intermediate) products such as ethylene oxide from ethanol. In a more mechanistic way, the use of Li_2O gave more

insight into the role of the different components. For methanol oxidation in chapter 4 it was proposed that the formed formaldehyde was an intermediate product in the total oxidation towards CO_2. Methanol was dehydrogenated to formaldehyde on the γ-Al_2O_3, which was further oxidized on the metallic particles. Due to the low O_2 concentration not all the formaldehyde could be oxidized to CO and CO_2. This same reaction showed that the catalytic activity of the silver based catalysts was somewhat different, as the silver particle were capable of formation of formaldehyde, probably due to the low oxidizing capabilities. In chapter 5 and chapter 6 dealing with ethanol oxidation and dehydrogenation the use of Li_2O gave more insight into the mechanism. In the dehydrogenation of ethanol ethylene oxide was formed in the first heating stage on the gold and copper based catalysts, which can be attributed to the metal particles. As in the following heating and cooling stage no ethylene oxide was formed due to coke formation, but acetaldehyde was formed, which again can be attributed to the gold and copper particles, it became apparent that these catalysts contain more than one catalytic active center.

8.3 Effect of CeO_x

CeO_x is a well-known co-catalyst, which can be used as a catalyst itself. One of the most active catalyst in oxidation reactions contain both Au and CeO_x. On this catalyst the reactant is activated on the gold and the cerium oxide is providing active oxygen. For this the structure and average size of the metal oxide is important. Indeed we found that for all investigated reactions and all used metals the addition of cerium oxide resulted in a catalyst with stronger oxidizing characteristics, and an increase in oxygen conversion. This resulted in higher selectivities towards CO and CO_2 despite the relatively low content of oxygen.

Gluhoi et al. found that addition of CeO_x in combination with Li_2O show a synergistic effect in the total oxidation of propene. This origin of this synergistic effect is not completely understood [4]. In the preferential oxidation of CO in chapter 2 indeed a synergistic effect was found not only for the gold based catalyst, but also the silver and copper based catalysts. However, for the other investigated reactions no synergistic effect was found.

8.4 Future prospects and recommendations

In the catalytic processes described in this thesis the interaction between the metal nanoparticles, the additives and the support is very important. Especially with the choice of additive the selectivity to certain products can be enhanced or decreased. The catalytic reaction is taking place on one of the components of the catalyst but when nanoparticles are used, the reaction is probably taking place at the interface of the metal and the support or additive. Results in this thesis make clear that with the used catalysts every added component has influence on the activity and the selectivity of the catalyst and the activity of the catalysts is dependent on the cooperation between all the components. If more insight is acquired in the effects that all the used components have on each other it might be possible to discover future catalysts more on basis of a general scientific approach, rather than trial and error.

The results described in this thesis, are very interesting and should be explored more extensively, especially in the dehydrogenation and oxidation reactions of the alcohols. In the following section a few suggestions are made:

- For the use of gold in catalysis the particle size is very very important. It only shows activity when the particles size is below 5nm. Other metals are also active when deposited as larger particles, but as chapter 2 and chapter 3 show: the effect of particle size is not unique for gold but also applicable for copper and silver. This raises the question, what the effect is on catalytic processes if very small particles of copper and silver are used instead of larger particles.

- In chapter 4 it became clear that the used γ-Al_2O_3 support from BASF is active in methanol dehydrogenation to formaldehyde. Other tested alumina supports show less activity. It is not completely clear if the activity in methanol dehydrogenation of the alumina from BASF is caused by the impurities of copper and/or iron or it is related to another characteristic of the γ-Al_2O_3. Therefore more research should be done concerning the reasoning why the used alumina is active.

- The chapters concerning the alcohols show that addition of Li_2O has a great influence on the catalysis. Not only in terms of particle size, but also in poisoning the acidic sites of the alumina. In the results described in this thesis, only one alkali metal was used. It is known that also other alkali metals can affect the acidic sites of alumina. Hence it should be interesting to investigate which effect of addition of other alkali metal oxides have on the selectivity.

- The amount of Li_2O used was about 10wt%. Compared to literature data this is a large amount. The question arises if the effect of Li_2O can be sustained if lower amounts are used.
- When gold and silver based catalysts are used in the conversion of ethanol into ethylene oxide it is possible to get high conversion rates and high selectivities. Although the results of chapter 5 and chapter 6 are very promising, there is already a well established process for producing ethylene oxide. It will be very hard to compete with that commercial process. A lot of research should be done to understand to optimize the performance of the catalyst to be able to develop this catalytic process in a economically successful process.
- In chapter 7 an exploratory study in the oxidation and dehydrogenation of propanol is described. As the results were not successful in terms of converting propanol into propylene oxide more research has to be done to investigate the possibility to produce propylene oxide with propanol as starting product, in line with the formation of ethylene oxide from ethanol.

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Summary

In this thesis several new insights and possibilities concerning gold catalysis are presented. One of the goals was to investigate the role of the Au particle size. For the activity of gold based catalysts, it is very important that the gold particles have a size below 5 nm. The question arises is this effect unique for gold catalysis or can a similar effect be found with the related metals silver and copper? Therefore the catalytic behavior of comparable copper and silver based catalysts were investigated. This was mainly done by testing the activity of the catalyst from room temperature up to 400 °C in the following reactions: selective oxidation of CO in chapter 2, ammonia oxidation in chapter 3 and the oxidation of methanol, ethanol and propanol in chapters 4,5,6 and 7. Also the composition and particle size of the catalysts are determined. Copper and silver were chosen as they chemically resemble gold. The effect of particle size is described in chapter 2 and 3. The results show that nanoparticles of copper and silver show different behavior or enhanced activity compared to larger particles and hence the particle size effect is important in copper and silver based catalysts.

When the active metals are deposited as nanoparticles, the catalytic activity is greatly influenced by the interaction with support and additives. In this thesis the role and interaction of Li_2O and CeO_x with the metal nanoparticles and support is investigated. Earlier, it was found that Li_2O acts as a structural promoter of gold by preventing sintering of the gold nanoparticles. In the studies described in this thesis this same effect was also found for the copper and silver based catalysts. However, it was found that the role of Li_2O is not solely the prevention of sintering but it also poisons the acidic sites, which are active in the catalytic reactions of alcohols, of the alumina support and so has a great influence on the activity and, especially, the selectivity of the catalysts. The addition of Li_2O results in a catalyst with is capable of converting ethanol with high selectivity to ethylene oxide, especially when low oxygen concentration of oxygen in the gas feed is used. This has not been reported before. The use of Li_2O, which poisons sites which are catalytic active, gave the

researchers more insight into the mechanism of the concerned reactions and several mechanisms could be proposed.

CeO_x is a well-known co-catalyst, which can be used as a catalyst itself. One of the most active catalyst in oxidation reactions contains both Au and CeO_x. On this catalysts the reactant is activated on the gold and the cerium oxide is providing active oxygen. Here the structure and average size of the metal oxide is important. Indeed we found that for all investigated reactions and all used metals the addition of cerium oxide resulted in a catalyst with stronger oxidizing characteristics, and an increase in oxygen conversion. This resulted in higher selectivities towards CO and CO_2 despite the relatively low content of oxygen used.

The results concerning the formation of ethylene oxide from ethanol on gold based catalysts motivated us the investigate the possibility of converting 1-propanol and/or 2-propanol directly to propylene oxide. This would be a very interesting reaction as there is no suitable catalyst for this process. In this exploratory study in chapter 7 we found that gold based catalysts are capable of converting propanol to acetone and propylene. Minute traces of propylene oxide are found. It is suggested that the conversion of 1-propanol to acetone and 2-propanol is proceeding via a propylene oxide intermediate.

Samenvatting

In dit proefschrift worden enkele nieuwe inzichten en mogelijkheden van het gebruik van goud in de katalyse gepresenteerd. Een van de doelen was het onderzoeken van het deeltjesgrootte effect. Voor de activiteit van goudkatalysatoren is het belangrijk dat de deeltjesgrootte onder de 5 nm is. Met behulp van het toevoegen van Li_2O en CeO_x aan eeen drager van alumina kan een stabiele katalysator met kleine gouddeeltjes gemaakt worden. Het is de vraag of dit effect van alleen voor goud geldt of ook voor andere vergelijkbare metalen zoals zilver en koper? Om deze vraag te beantwoorden is de katalytische activiteit van vergelijkbare koper en zilver katalysatoren onderzocht. Dit is voornamelijk gedaan met behulp van activiteitsmetingen van kamertemperatuur tot 400 °C. Bij de volgende reacties: selectieve oxidatie van CO in hoofdstuk 2, ammonia oxidatie in hoofdstuk 3 en de oxidatie van methanol, ethanol en propanol in hoofdstukken 4,5,6 en 7. Ook de samenstelling en deeltjesgrootte werden gemeten. Het deeltjesgrootte effect is onderzocht in hoofdstuk 2 and 3. De resultaten laten zien dat, vergeleken met grotere deeltjes, het effect van nanodeeltjes resulteert in verhoogde activiteit en een andere selectiviteit. Dus ook bij koper en zilver is, een vergelijkbaar deeltjesgrootte effect als bij goud, aangetoond.

Wanneer het actieve metaal in de vorm van nanodeeltjes wordt afgezet op een drager, is de interactie tussen metaal en de drager en toevoegingen erg belangrijk voor de katalytische activiteit. In dit proefschrift is de interactie tussen lithiumoxide en ceriumoxide en de drager en metaal onderzocht. Bij eerdere studies was al ontdekt dat Li_2O een structurele promotor is en voorkomt dat de kleine gouddeeltjes groter worden. De resultaten van dit proefschrift laten zien dat hetzelfde gebeurt bij toevoeging van lithium oxide bij koper en zilver deeltjes. De resultaten laten echter ook zien dat Li_2O ook nog een andere rol heeft. Het deactiveert ook de zure sites van het aluminiumoxide die actief zijn in de katalyse van alcoholen. Deze deactivering is dan ook van grote invloed op selectiviteit van de katalysatoren. Door toevoeging van lithium oxide kan een katalysator gemaakt worden die in staat is om ethanol in een zuurstofarme omgeving om te zetten naar etheenoxide met hoge selectiviteit. Dit

is nog niet door iemand anders eerder gerapporteerd. Door het gebruik van lithiumoxide kregen de onderzoekers meer inzicht in de mechanismes van de reacties en konden enkele mechanismen worden uitgelegd.

Ceriumoxide wordt in de katalyse veel gebruikt, als toevoeging maar ook als katalysator. Een van de meest actieve katalysatoren in oxidatiereacties bevat ceriumoxide en goud. Bij deze katalysator wordt de reactant geactiveerd op het goud en levert het ceriumoxide geactiveerd zuurstof voor de reactie. Hierbij is de deeltjesgrootte en de structuur erg belangrijk. In de reacties die in dit proefschrift zijn onderzocht is inderdaad gevonden dat toevoeging van ceriumoxide een katalysator oplevert die sterker oxiderend is, waardoor er meer CO en CO_2 gevormd wordt.

De resultaten die zijn gevonden bij de vorming van etheenoxide uit ethanol op goudkatalysatoren zetten ons aan om te onderzoeken of een vergelijkbare reactie mogelijk was met als uitgangsproducten 1-propanol en 2-propanol. Dit zou dan propeenoxide kunnen opleveren, wat een commercieel interessante reactie is, aangezien er voor dit product nog geen geschikte katalysator is. Via deze katalytische reactie wordt nauwelijks propeenoxide gevormd als eindproduct, maar mogelijk wordt het wel als tussenproduct gevormd en reageert dan weer verder.

Nawoord

Eindelijk! Dat zal bijna iedereen denken. En terecht. De tijdspanne waarin dit proefschrift tot stand is gekomen is langer dan gemiddeld. Bijna op de dag af is het 10 jaar geleden dat ik begon als assistent in opleiding. In die tien jaar is er veel gebeurd, bijvoorbeeld bij de vakgroep: Iedereen die in 2001 deel uitmaakte van de surfcat groep is nu of ergens anders naar toe gegaan of hebben de pensioen gerechtigde leeftijd bereikt. (Voor Karlien: in 2010 was dat al bij 65 jaar).

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Iedereen bedankt!!!
Meindert
Leiden, oktober 2010

CV

Schrijver dezes is geboren op dinsdag 18 maart 1975 te Geldrop, Noord-Brabant. Zijn schoolopleiding is begonnen in Geldrop. Via de peuterspeelzaal en de kleuterschool ging hij in 1981 naar de lagere school *Margartha Sinclair*, die inmiddels is opgedoopt naar *Windroos*. De opleiding werd vervolgt in Eindhoven aan het *Augustiniuanum*. Eerst op de gymnasiale afdeling, maar via een doublure in de derde klas werd het atheneum in 1994 afgerond met 11 vakken. De volgende stap was de universiteit van zijn ouders: *de Rijksuniversiteit Leiden*,(tegenwoordig de *universiteit Leiden*). Hier werd een studie scheikunde begonnen (tegenwoordig Molecular Science and Technology) en deze langstudeerder heeft de studie afgerond (via een regulier traject) in 2001 met de specialisatie Heterogene Katalyse (tegenwoordig is deze vakgroep opgeheven). Daaropvolgend is hij van 2001 tot en met 2008 gaan werken als assistent in opleiding bij het *Leids instituut voor chemisch onderzoek* van de *Universiteit Leiden*, in de groep van Ben Nieuwenhuys. Dit proefschrift beschrijft het in die peeriode verrichte onderzoek. Per 2007 is hij verbonden als docent chemie aan het cluster techniek van de hogeschool leiden

Stellingen

Behorende bij het proefschrift
Catalytic behavior of Cu, Ag and Au nanoparticles
A comparison.

1 Een belangrijk verschil tussen grote bulkdeeltjes en nanodeeltjes, afgezet op een drager, is dat bij nanodeeltjes meer atomen met verschillende coördinatie aan de oppervlak voorkomen, zodat meerdere katalytische active sites worden gecreëerd. *Dit proefschrift, hoofdstuk 6*

2 In de literatuur is nog steeds veel discussie over de lading van de actieve gouddeeltjes. Dit wordt mede veroorzaakt omdat de mogelijkheid van meerdere soorten actieve deeltjes zelden wordt onderzocht. *Dit proefschrift, hoofdstuk 6*

3 De in deze dissertatie beschreven resultaten met betrekking tot de oxidatie van methanol tonen aan dat onderzoek naar het gedrag en activiteit van de drager en additieven soms belangrijker is dan het onderzoek naar het metaaldeeltje. *Dit proefschrift, hoofdstuk 4*

4 Bij de conclusies die Gang et al. trekken op basis van hun resultaten voor de verschillende activiteit en selectiviteit gaan ze voorbij aan de mogelijke effecten van het verschil in deeltjesgrootte van het zilver.

L. Gang *et al.* Appl. Catal. B 40 (2003) 101.
Dit proefschrift, hoofdstuk 3

5 Het is erg gevaarlijk om te stellen dat de hoge activiteit van goud bij lage temperaturen uniek voor goud is, als vergelijkbare gegevens voor alle andere metalen niet beschikbaar zijn.

G. Hutchings, Gold Bulletin 2004.
Dit proefschrift, hoofdstuk 2

6 Na twintig jaar onderzoek naar nanodeeltjes is er nog steeds geen duidelijke definitie van een ”nanodeeltje”. Aangezien daar geen wetenschappelijke oorzaak voor is, is de reden hiervoor waarschijnlijk financieel van aard.

7 Het is merkwaardig dat L. Zhang *et al.*, in hun metingen naar de selectieve oxidatie van ammonia naar stikstof, uitspraken doen over de selectiviteit naar stikstof zonder dat ze het stikstofgehalte kunnen meten, aangezien zij de voor het infraroodgebied niet zichtbare stikstof bepalen met een FTIR.

L. Zhang, C. Zhang, H. He, J. Catal. 261 (2009) 101.

8 Veel auteurs beweren dat de bereidingswijze van gedragen goud katalystoren van invloed is op de katalytische activiteit. Dit is niet correct. Ze zouden moeten beweren dat een bepaalde bereidingsmethode meer geschikt is dan een andere, om een katalystor te maken met de optimale dimensies voor de onderzochte reactie.

L. Jinwei *et al.* J. of rare earths, 28 (2010) 547
D. Andreeva *et al.* Appl. Catal. A, 357(2) (2009) 159.

9 De conclusie van L. Jinwei *et al.* dat de optimale goudlading 2-3wt% is, is aan twijfel onderhevig. Aangezien zij niet hogere goudladingen hebben onderzocht, kunnen zij alleen stellen dat de katalystoren met een goudlading van 2-3wt% een hogere activiteit vertonen dan katalysatoren met een lagere goudlading.

L. Jinwei *et al.* J. of rare earths, 28 (2010) 547

10 De belangrijkste winst van de opleiding SMST t.o.v. de ”oude” opleiding scheikunde is de toevoeging van het vak chemische analyse methoden.

11 Dat God zonder televisie zo bekend is geworden is het echte Godsbewijs.

12 Vroeger dreigden ze met hel en verdoemenis, nu met milieu, vergrijzing en pensioen

13 Bij iedere onderwijsvernieuwing wordt vergeten op schoolniveau voldoende tijd en geld beschikbaar te maken om de vernieuwing in te voeren.

Meindert Lippits